Polysiloxane supported metal catalysts

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POLYSILOXANE SUPPORTED METAL CATALYSTS

A Thesis submitted by Andrew M. Watts

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DEDICATION

To

My Parents.

ACKNOWLEDGEMENTS

I would like to express my grateful thanks to Dr. B.J. Brisdon for his advice and guidance throughout this work, and in the preparation of this thesis.

I would also like to record my thanks and appreciation to the Staff of the School of Chemistry, Technicians and fellow Students.

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SUMMARY

A range of tri-, tetra-, and penta-siloxanes of general formula $Me_3SiO\left[SiMe(R)O\right]_nSiMe_3$ (R = vinyl, n = 1 - 3; R = an alkyl chain terminated by the potential metal-ligating entities $CH{=}CH_2$, CN, PPh_2, n = 1 - 3; Ph, cyclohexenyl, hydrido, n = 1 and 2; R = SPh, Br, pyridine, n = 1) have been synthesised from commercially available dichlorosilanes by one of three procedures. A more limited range of cyclosiloxanes $\left[SiMe(CH_2CH_2R)O\right]_4$ (R = Br, PPh_2) have been prepared by chemical modification of $\left[SiMe(CH{=}CH_2)O\right]_4$.

Linear polysiloxanes of general formula $Me_3SiO\left[(SiMe_2O)_xSiMe(R)O\right]_nSiMe_3$ (R = vinyl, hydrido or an alkyl chain terminated by Br, Ph, CN, PPh_2) were synthesised from the acid catalysed polymerisation of $(SiMe_2O)_4$ and $(SiMe_3)_2O$ with either a functionalised dichlorosilane precursor (for R = Ph, CN and H), or with the vinyl cyclosiloxane $\left[SiMe(CH{=}CH_2)O\right]_4$, followed by chemical modification (for R = Br and PPh_2).

To the model functionalised siloxanes, cyclosiloxanes and linear polysiloxanes a variety of transition-metal species have been anchored under mild reaction conditions. These include the metallic moieties MCl_2 (M = Ni, Pd, Pt), $Fe(CO)_4$, $Mo(CO)_3$, $Mo(CO)_4$, RhCl, Rh(CO)Cl, $Rh(CO)_2Cl$ and $H_2Os_3(CO)_{10}$.

The metallated and non-metallated compounds were characterised by conventional analytical techniques, including nuclear magnetic resonance spectroscopy, infrared spectroscopy, mass spectrometry, gel permeation chromatography and elemental analysis where possible.

A limited number of metallated model siloxanes and polysiloxanes were tested for activity as hydrogenation and hydrosilylation catalysts for reactions with olefin substrates.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS

b.p.	boiling point
bipy	2,2'-bipyridine
COD	cycloocta-1,5,-diene
D	difunctional
DMF	dimethylformamide
DVB	divinylbenzene
ESCA	Electron Spectroscopy for Chemical Analysis
EXAFS	Extended X-ray Absorption Fire Structure
GPC	Gel Permeation Chromatography
h	ultraviolet irradiation
I	spin isotope
INEPT	Insensitive Nuclei Enhancement Polarisation Transfer
L	ligand
M	monofunctional
Me	methyl
MeCN	methylcyanide
mm Hg	millimeters of mercury (pressure)
mmol	millimol
Mw	molecular weight
N	nitrogen
n/i	normal to iso ratio
NBS	N-bromosuccinimide
Ph	phenyl
PhCN	phenylcyanide
Ⓟ	polymer support
PPh_2	diphenylphosphine
py	pyridine

Q	tetrafunctional
rt	ambient temperature
SIL	silica
SLPC	supported liquid phase catalyst
T	trifunctional
thf	tetrahydrofuran
TFMSA	trifluoromethylsulphonic acid
TMEDA	tetramethylethylenediamine
γ	gyromagnetic ratio

Infrared (IR) spectra:

cm^{-1}	wavenumber
m	medium
s	strong
sh	shoulder
v	very
w	weak
ν	stretching vibration

Nuclear Magnetic Resonance (n.m.r.):

d	doublet
J	coupling constant (Hz)
m	multiplet
OFR	off frequency resonance
ppm	parts per million relative to TMS
q	quartet
s	singlet
t	triplet
δ	chemical shift
TMS	tetramethylsilane

CHAPTER ONE

INTRODUCTION

1.1 GENERAL CONSIDERATIONS ON CONVENTIONAL AND SUPPORTED CATALYSTS

For many years, catalysts have been classified as either homogeneous or heterogeneous, with many systems being developed for a wide range of applications in both small and industrial scale processes. Homogeneous catalysts have been developed whereby a specific chemical compound is introduced into the reaction under study as a well-defined species, and operates through the formation of intermediate compounds. These catalysts generally function in solution, and have good solubility in the reaction medium. Heterogeneous catalysts are usually solids, and promote reaction by adsorption of reactants onto the catalyst surface.

Homogeneous catalysts have a number of limitations in their use, which include:

i) separation of the catalyst from the products at the conclusion of the reaction,

ii) the instability of some catalytic systems under operating conditions,

iii) the possibility of corrosion within the reaction vessel by catalytic solutions.

Heterogeneous catalysts often suffer from low activity and selectivity in reaction. Also, limitations are imposed on their future improvement due to ill-defined active sites and frequently unknown reaction mechanism. However, the advantages of these catalysts include:

i) high activity for a wide range of reactions,

ii) ease of separation from reaction products,

iii) good mechanical and thermal stability which permits their use in packed and fluidised beds, and at elevated temperatures and pressures.

In contrast, homogeneous catalysts are typified by:

i) high activity under mild reaction conditions,

ii) reactivity which has been interpreted and mechanised,

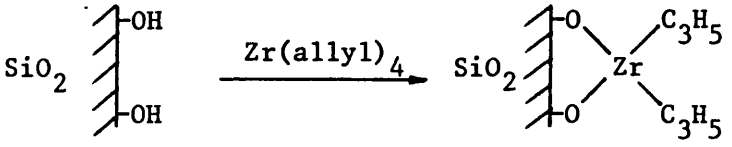
iii) high efficiency, specificity and reproducibility.

Thus, it would be beneficial to have a superior, active catalytic system possessing the advantages of both traditional catalysts with few of their disadvantages, and in the late 1960's the concept of anchoring transition-metal complexes onto support matrices to produce hybrid catalysts was evolved. A principal motivation of this technique was to facilitate recovery of the catalyst from the reaction medium, for example, by filtration.

There is no defined designation for catalysts prepared on the basis of immobilising transition-metal complexes in or on matrices, and references to "hybrid", "heterogenised-homogeneous" and "supported organometallic" have been made in the literature. No one term has been used exclusively owing to the various methods of preparation of such catalysts. The concept of hybrid catalysts reflects the idea of "an ideal" catalyst where all atoms of the transition metal should participate in the formation of active centres which are uniform and show total selectivity for the required reaction. The interest in this research area was significantly influenced by results reported at the V International Congress on Catalysis[1], and similarly at other symposia.[2] This area is currently attracting widespread attention with a number of books[3], reviews[4-8] and articles[9,10] having been published.

The process of heterogenisation may be accomplished in three main ways:

i) By attachment through chemical bonds of a metal complex to a support. For example, through surface silanol groups, π-allyl complexes may be supported on silica,[11-13] i.e.



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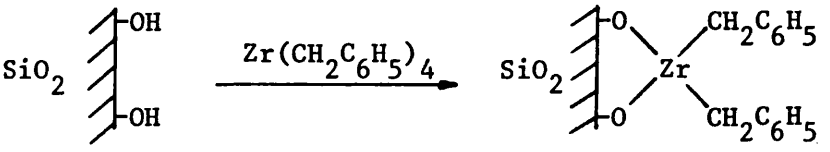
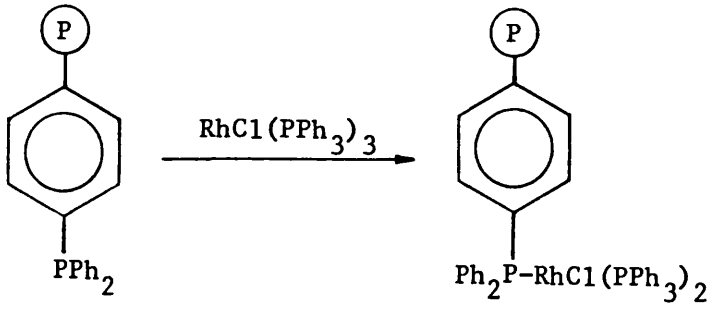


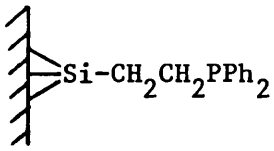
(2)

This technique has been referred to as "grafting" and is somewhat analogous to the reaction of a moisture sensitive organometallic with an alcohol. This class of catalyst may be extremely air and/or moisture sensitive in view of the high reactivity of metal-carbon bonds. Alternatively, insoluble organic polymers either bearing metal anchoring ligands or capable of being chemically modified may be used, e.g. diphenylphosphinated polystyrene.



(3)

Polymers for use in this type of anchored catalyst are now commercially available in bead form with controlled channel dimensions to increase their selectivity. A further approach involves the use of functionalised inorganic supports (e.g. silica) to the surface of which ligands may be attached often via phosphine groups, e.g.



(I)

In principal all these methods allow the chemical identity of some of the ligands around the metal centre to be retained during the heterogenisation step.

ii) Physical dispersion of a metal complex or ion within the pore structure of a support (e.g. silica) to produce dry or solid supported materials can be achieved by sintering or by evaporation of a solution containing the complex and carrier.

iii) By a similar procedure, supported liquid phase (SLP) catalysts can be prepared as in (ii) above but with a second relatively involatile solvent which remains dispersed in the solid after the volatile solvent has evaporated. These systems have only received limited attention.[14]

Irrespective of the method used, the support should be chemically inert to solvent and reagents during the catalytic reaction,

and have a high surface area. For both inorganic and organic polymer supports, the ligands used in anchoring must coordinate strongly and preferably give rise to complexes having high thermal stabilities, whereas non-anchoring ligands should aid solubility without sterically hindering approach to the active sites. An important aspect of an active catalyst is a coordinately unsaturated metal atom having one or more orbitals available for facile substrate coordination, and this can occur through an inherent electronic feature of the metallo-species or through the type of ligand dissociation processes which occur in homogeneous systems.

1.1.1. ORGANIC POLYMER SUPPORTS

The fundamental requirement for an organic polymer support is the incorporation of functional groups that are potential ligands, and examples of these polymers which have inherent functionality and are readily available include polystyrene, polyamides, acrylic polymers and poly(amino acids). Polystyrene has been the most frequently used because of its commercial availability in a number of forms, its inertness to chemical attack, and the relative ease with which it may be chemically modified to bear pendant ligands capable of anchoring transition-metal complexes.

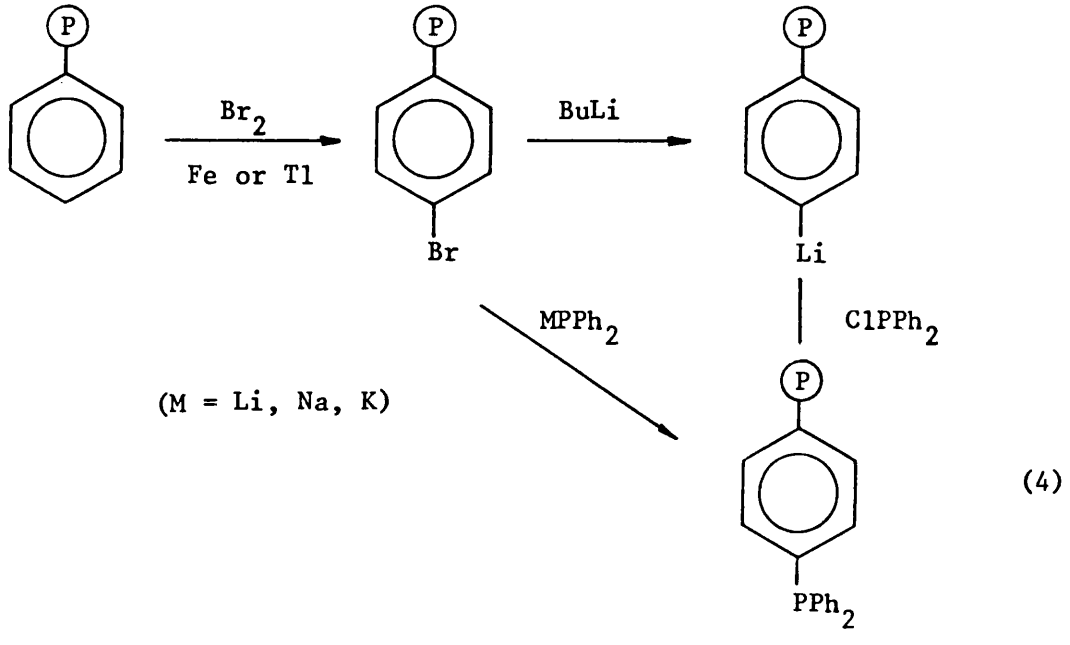
Polystyrene is prepared by polymerising styrene in the presence of a cross-linking agent, typically p-divinylbenzene (DVB). The degree of cross-linking determines the type of polymer and for 2% DVB a gel-type (microporous) polystyrene results which can swell and open all of its

internal volume to both solvent and reagent. This is essential for the anchoring step and for their use as catalysts. For polystyrenes with a high degree of cross-linking (typically up to 60% DVB), macroreticular or macroporous resins having high surface areas are formed. These resins restrict diffusion into the interior and anchored species are normally found in a thin layer at the internal surface. This rigidity within the resin can enhance catalytic activity[15] by reducing the possibility of dimerisation between active centres which subsequently causes deactivation.

The preparation of ligand-polymers can be readily achieved by either chemically bonding ligand groups to a preformed polymer, or by polymerising an available or preformed ligand-monomer. Several routes[16-18] have been devised for bonding tertiary phosphine groups to polystyrene, as described in the following schemes.

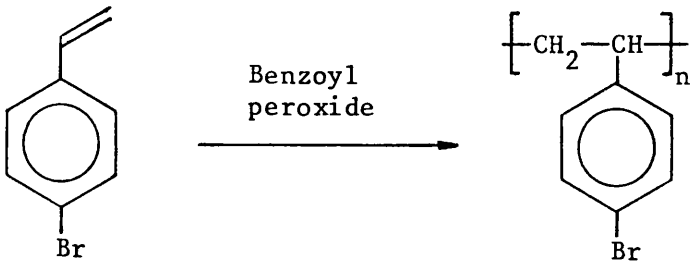
Scheme 1.

Bromination of a phenyl group is followed by either metallation and subsequent treatment with chlorodiphenylphosphine, or by direct phosphination with the diphenylphosphide anion.



(4)

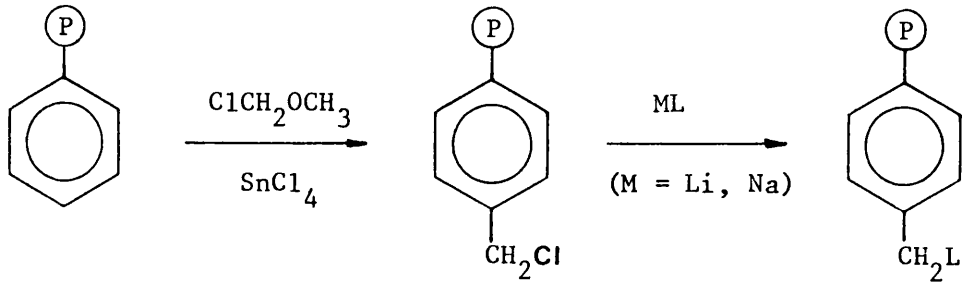
The lithiation step is commonly used in the preparation of polystyrene derivatives,[19] for example, the introduction of bipyridine.[20] Alternatively, brominated polystyrene can be prepared by the polymerisation of p-bromostyrene in the presence of benzoyl peroxide.[18]



(5)

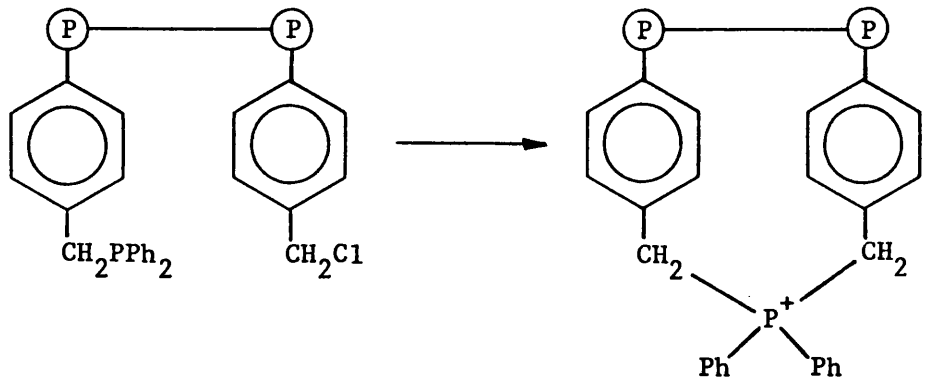
Scheme 2.

For unsubstituted polystyrene, introduction of a p-chloromethyl group[21] by treatment of an aryl group with chloromethyl methylether in the presence of stannic chloride facilitates an entry for ligands other than tertiary phosphines, such as cyclopentadienyl,[22] acetylacetonate,[23] or isonitrile moieties.[24]



(6)

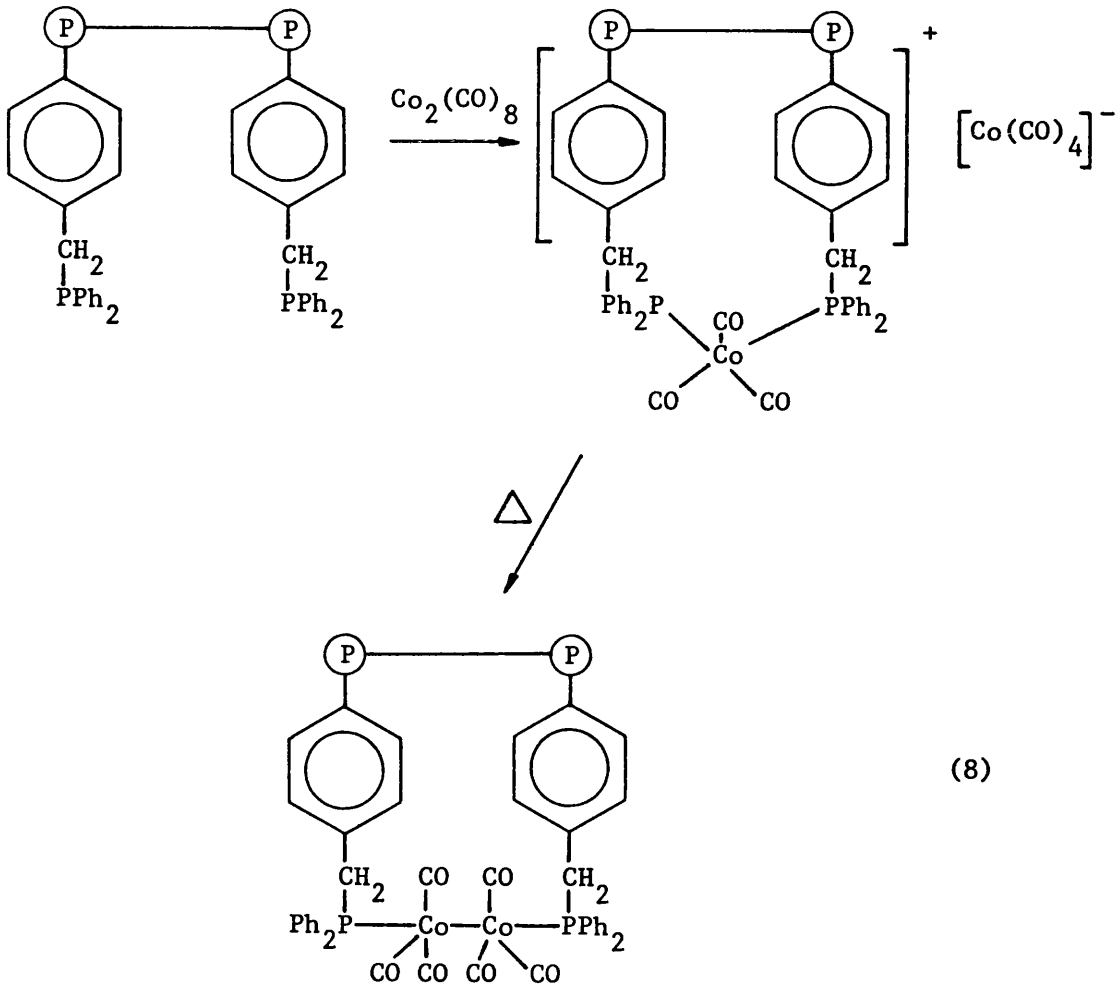
It is essential that halogen replacement is complete to avoid quaternisation when L is a phosphine, i.e.



(7)

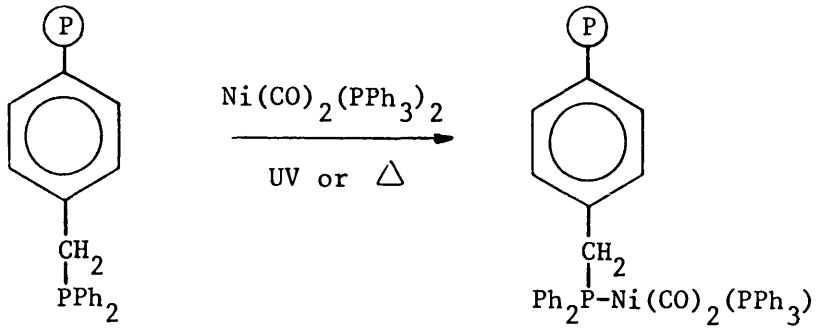
Although phosphine moieties have been used extensively for anchoring metal complexes, amine groups are becoming increasingly common. Amine functionalised polystyrenes and polymethacrylates have been prepared, and after complexation serve as active catalysts for hydrosilylation, hydroformylation and hydrogenation reactions.[25]

Whilst polystyrene has received most attention as an organic polymer support, alternative polymers are available and include polyvinylalcohol,[18] polybutadiene,[18] polymethacrylate allylchloride/DVB.[25] polyvinylchloride,[26] polyphenylene-isophthalamide[27] and poly-4-vinylpyridine.[28] Once functionalised, direct coordination of a metal complex to the support by use of thermal or photochemical techniques generally yields an active catalyst which can be used in one or more catalytic systems. Pittman et al[15] has used such methods to prepare active hydroformylation catalysts, e.g.



(8)

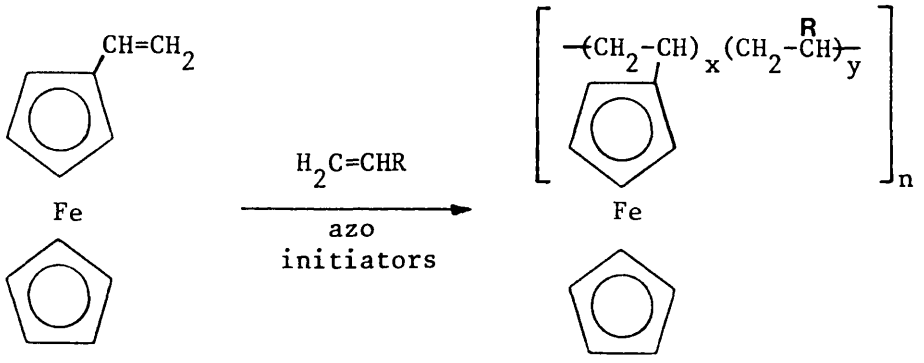
In the same communication Pittman et al illustrated another method for anchoring catalysts using a phosphine ligand exchange reaction. The following reaction employing a nickel carbonyl phosphine species generates an active oligomerisation catalyst.



(9)

Reference to Hodge and Sherrington's book illustrates the range of ligands which can be used in conjunction with different types of supports, and gives examples of catalysts derived from them. Table 1.1 lists a number of such examples for functionalised polystyrenes.

As an alternative to anchoring metal complexes on preformed organic polymeric supports, Pittman[39] has also synthesised metal containing monomeric entities which can be polymerised into polymeric analogues, e.g. polymerisation of vinyl ferrocene.



(10)

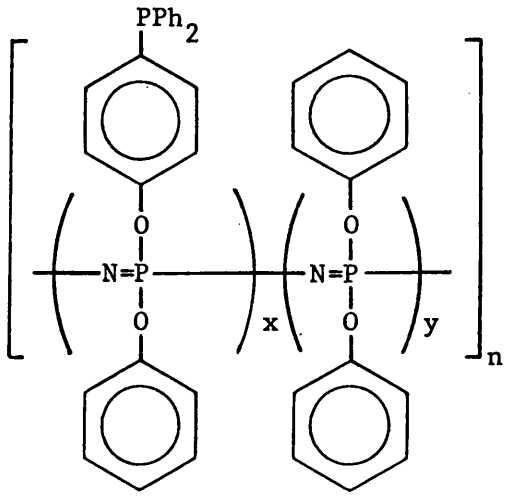
Although such systems have interesting synthetic applications, no pronounced catalytic activity has been found to date.

Table 1.1 Examples of polystyrene supported catalysts with indication of their catalytic action

Functionality	Metal complex	Catalytic action	Reference
PPh_2	$[RhCl(C_2H_4)_2]_2$	Hydrogenation	29
PPh_2	$PtCl_2$	Hydrogenation	30
PPh_2	$Rh(acac)(CO)_2$	Hydroformylation	18
PPh_2	$[Rh(CO)_2Cl]_2$	Hydroformylation	31
		Carbonylation	116
		Ethanol-^2H exchange	32
PPh_2	$NiCl_2$	Polymerisation	33
PPh_2	$RhCl_3$	Hydrosilylation	34
C_5H_5	$TiCl_2$	Hydrogenation	15
CN	H_2PtCl_6	Hydrosilylation	35
NMe_2	H_2PtCl_6	Hydrosilylation	36
Br	$Ni(PPh_3)_4$	Dimerisation	37
No further functionalisation	$Cr(CO)_6$	Hydrogenation	38

The types of supported catalyst discussed so far are generally insoluble in common solvents, and their resultant activity is dependent upon solvation of the anchored metal entity. Bayer and Schurig[40] have used phosphine functionalised noncross-linked polystyrene as a soluble polymer support, and active hydrogenation and hydroformylation catalysts using $RhCl(PPh_3)_3$ and $t\text{-}Rh(CO)Cl(PPh_3)_2$ respectively have been prepared. These systems reduce the non-equivalence of active sites arising from conformational changes which can occur on swelling of insoluble cross-linked polmers. A further advantage arises from the ease with which substrates can access to the catalytic site. Separation of the soluble polymer supported homogeneous catalysts form the reaction mixture can be achieved using membrane filtration or precipitation techniques.

Recently another type of macromolecular support utilising phosphines poly(organophosphazenes) has been reported in the literature.[41] Initial studies were on cyclic trimeric phosphazenes (II) which served as model compounds for their polymeric analogues, and for both classes a range of transition-metal complexes have been anchored to these substrates.



$n \approx 7000$

(II)

Very recently, Jones and Seeberger[42] have reported a new method for anchoring transition metal species such as $\left[Rh(COD)Cl\right]_2$ and $Pt(COD)Cl_2$ to polymers through phosphido type linkages, and have commented on their use as hydrogenation catalysts. However, the actual coordination geometry of the metals in these systems is unknown and the metal complex attachment to the polystyrene support is only assumed to be via phosphido moieties.

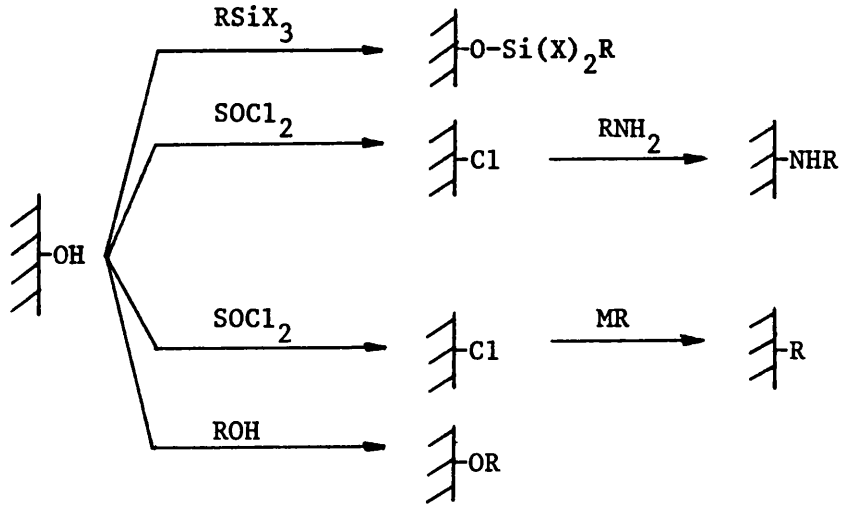
From the organic polymeric materials reviewed, most systems have hydrophobic character and are not compatible with polar and aqueous media. A number of reports have appeared in the literature on hydrophilic resins, but their syntheses are generally not easy.[43,44] However, Arshady and Corain[45] have synthesised a polymer support carrying the isonitrile functionality, and have used this material to coordinate several transition-metal centres in the presence of polar solvents such as dichloromethane and water.

1.1.2 INORGANIC OXIDE SUPPORTS

Inorganic oxides have frequently been used as macromolecular support materials, especially derivatives of silica,[46] silica-alumina mixtures and zeolites,[48] and only these will be considered further. Although most inorganic oxide supports possess active surface groups which can for example immobilise transition-metal carbonyls, the surface silanol groups are more usually used for bonding metal anchoring functional groups. Functionalisation using surface hydroxyl groups has been used in modifying chromatographic column substrates.[49] For oxide immobilised catalysts, side reactions on the support itself are

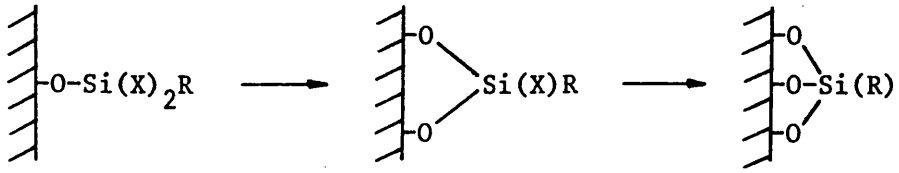
possible and proved to be a frequent disadvantage. This can be reduced by modifying the surface hydroxyl groups with a silylating agent, for example trimethylchlorosilane, to give a surface layer lipophilic in nature without significantly altering the catalytic activity.[50]

Although there are several methods of attaching ligand groups to inorganic surfaces, the most viable route usually involves reaction of a readily hydrolysable moiety with a surface hydroxyl group to attach ligand functions through covalent bonds.



(11)

The first route (via $RSiX_3$) has been used most frequently since one or more very strong Si-O-Si links are formed, and the Si-C bond at the surface has greater hydrolytic and thermal stability than Si-O-C or Si-N-C links.



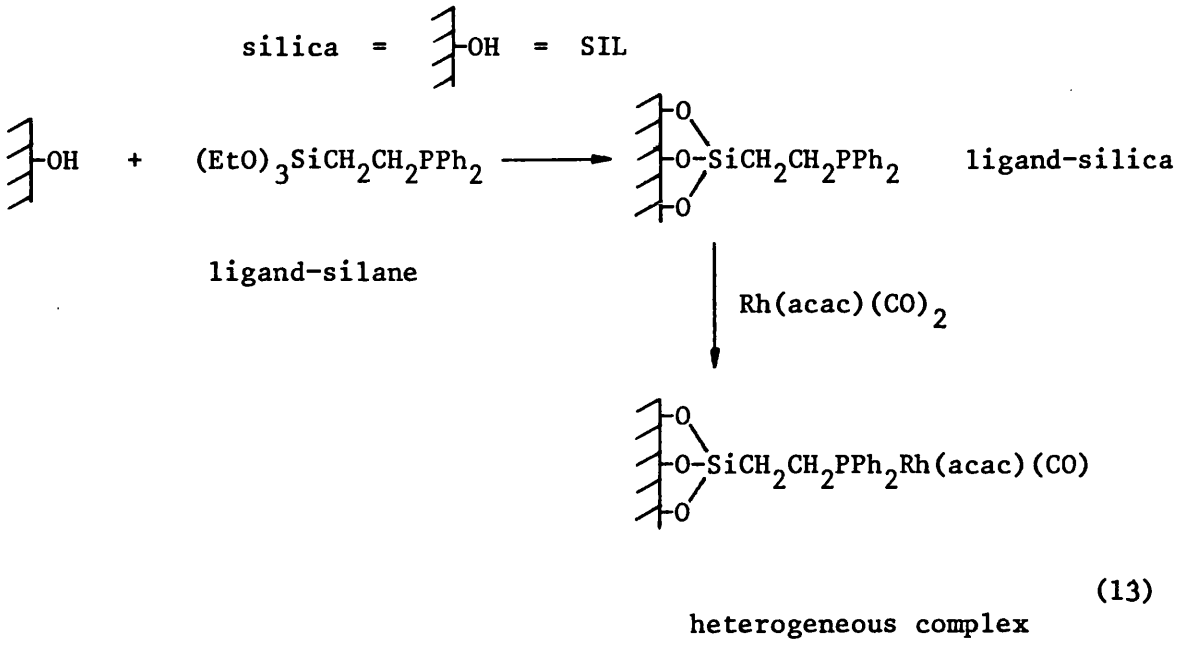
(12)

Generally, silicon alkyl-carbon bonds are preferred to silicon aromatic-carbon bonds because of their particular stability. The condensation reaction between a molecule containing an Si-X bond and a silica surface has been studied in both the gas and liquid phases, and the reaction appears to occur more rapidly in the condensed phase.[50] This reaction has been achieved with numerous inorganic surfaces besides silica, including glass,[52] and diatomaceous earths.

A large range of $RSiX_3$ type compounds are commercially available and have been used to anchor phosphines, amines and the cyclopentadienyl moiety for example, using this simple one-step condensation reaction. Of particular interest has been 2-(diphenylphosphine)ethyltriethoxysilane $\left[(EtO)_3SiCH_2CH_2PPh_2\right]$, and 3-aminopropyltriethoxysilane $\left[(EtO)_3SiCH_2CH_2CH_2NH_2\right]$. The former can be prepared by the ultra-violet irradiation of diphenylphosphine and vinyltriethoxysilane according to Niebergall's procedure[51] :

$$Ph_2PH + H_2C{=}CHSi(OEt)_3 \xrightarrow{h\nu} (EtO)_3SiCH_2CH_2PPh_2$$

Many groups of workers, notably the British Petroleum researchers, have prepared ligand-functionalised silicas[50, 52-56] using this compound as a metal anchoring ligand either prior to or after attachment to silica, and heterogeneous complexes incorporating a range of transition-metals have been prepared.[57-60] The following schemes illustrate how the heterogeneous complex can be formed.



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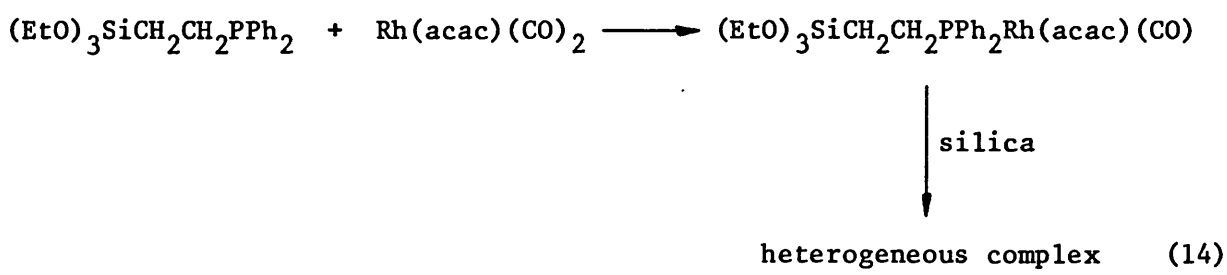
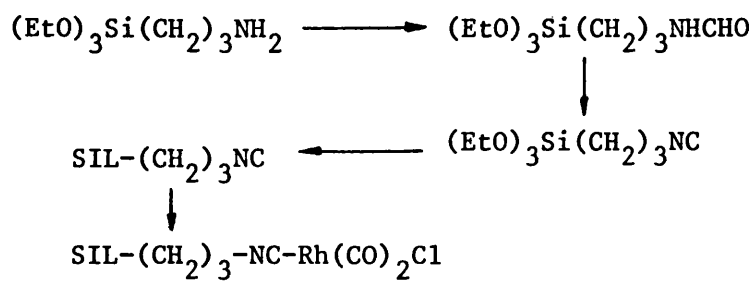


(14)

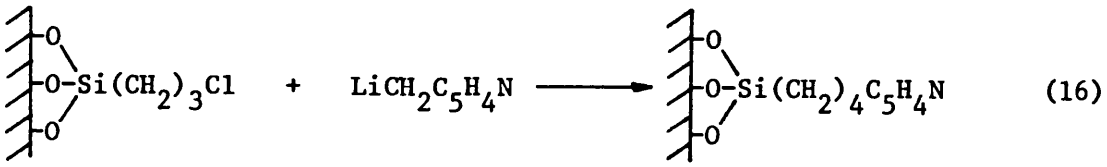
3-aminopropyltriethoxysilane may be used as a precursor for further end-group functionalisation or directly as a metal anchoring ligand when bound to silica. Howell and Berry[24] have utilised this silane to good effect in preparing an isonitrile functionalised silica which readily reacts with $\left[Rh(CO)_2Cl\right]_2$ to form the $Rh(CO)_2Cl(-NC)$ complex.



(15)

More recently, and using similar procedures, a Chinese group of workers have prepared active hydrogenation catalysts using palladium complexes supported on poly-y-cyano and aminopropylsiloxanes,[61] and a hydrosilylation catalyst composed of a silica supported poly-y-mercaptopropylsiloxane platinum complex.[61]

Another method of introducing ligand entities involves reaction of a chloroalkyl-silica surface with reagents such as $LiPPh_2$ or $LiCH_2C_5H_4N$ to produce diphenylphosphine and pyridine derivatives respectively.



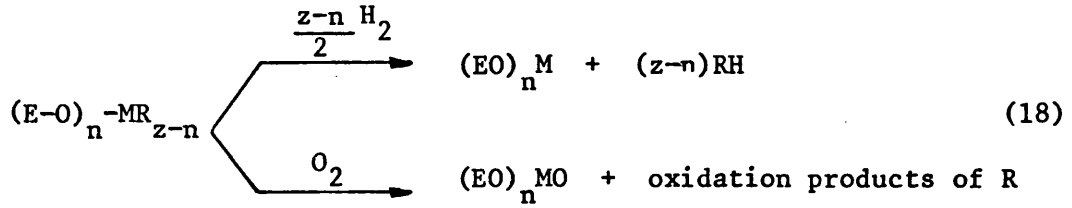
A summary of catalysts based on functionalised silica is presented in Table 1.2.

Silica surfaces have also been used to prepare grafted catalysts where a transition metal is bound directly to surface oxygen ions. The following scheme by Yermakov,[12] describes general procedures for their preparation.

$$(E\text{-}OH)_n + MR_z \longrightarrow (E\text{-}O)_nMR_{z-n} + nRH \qquad (17)$$

(where E is the element forming an oxide)

The supported metals can then be either reduced to low valent ions of transition metals, or oxidised to higher valency states:

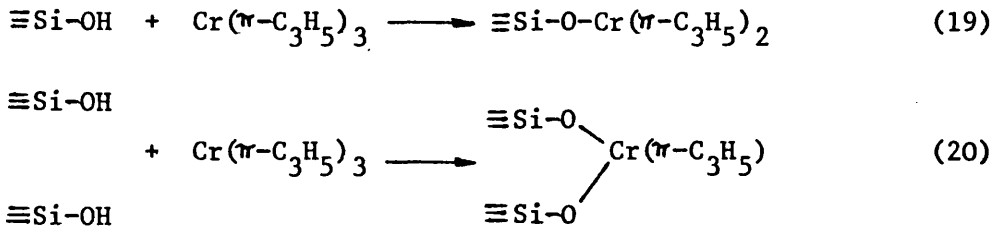


(18)

Table 1.2 Examples of silica supported catalysts with indication of their catalytic action

Functionality	Metal complex	Catalytic action	Reference
Phosphinated	$[RhCl(C_2H_4)_2]_2$	Hydrogenation	63
Phosphinated	$[IrCl(COD)_2]_2$	Hydrogenation	64
Nitrile	$[Rh(CO)_2Cl]_2$	Hydroformylation	53
Pyridine	$[Rh(CO)_2Cl]_2$	Hydroformylation	53
Nitrile	H_2PtCl_6	Hydrosilylation	65
Phosphinated	$PdCl_2$	Acetoxylation	64
Phosphinated	$Ni(COD)_2$	Polymerisation	64

Specific examples by Yermakov *et al* using silica show that the interaction proceeds through the participation of one or two silanol groups, i.e.



(19)

(20)

The final activity of this catalyst is largely determined by the preliminary dehydration temperature (T_d) of the silica used. The effect of T_d controls the amount of metal that can be bound, and when optimum T_d has been passed the level of metal loading is reduced through loss of OH groups.

A range of metals including Ti, Zr, Cr, Ni, Mo, W, Pd and Pt have been grafted onto oxide supports to yield catalysts capable of facilitating olefin disproportionation, polymerisation and catalytic hydrogenation. Molybdenum supported catalysts such as $(\equiv SiO)_2Mo(\pi\text{-}C_3H_5)_2$ have shown activity in olefin disproportionation reactions, and on reduction of the transition-metal complex with hydrogen a catalyst that can be used to hydrogenate ethene over a temperature range of -78 to + 200°C results.[12]

Another type of support has been developed by Rony[62] in which homogeneous catalysts are impregnated on a porous surface. Besides silica, alumina and activated carbon have also been exploited as supports,[14] while the catalysts have been prepared from $RhCl(PPh_3)_3$, $RhCl_3.3H_2O$ and $Rh(CO)Cl(PPh_3)_2$ for hydrogenation, isomerisation and hydroformylation studies respectively. For the isomerisation of but-1-ene to cis-and trans-but-2-ene, and the hydroformylation of propene to n- and iso-

butyraldehyde, Rony found greater activity for supported liquid phase catalysts as opposed to their solid supported counterparts, and he attributed this behaviour to higher molecular dispersion in the former case. However, for the hydrogenation of propylene using $RhCl(PPh_3)_3$ superior activity was found for the solid supported catalyst.

Silicates such as montmorillorite and hectorite have been used to immobilise cationic transition-metal complexes, and the resulting systems have shown activity towards hydrogenation and hydroformylation reactions.[66,67] Choudary *et al*,[68] have extended the use of montmorillorite to anchor palladium chloride through pendant phosphine ligands, and this particular species has been found to hydrogenate terminal alkenes and alkynes selectively. The authors studies also give an example of the routine use of X-ray photoelectron spectra to determine the valency state of the coordinated metal atoms.

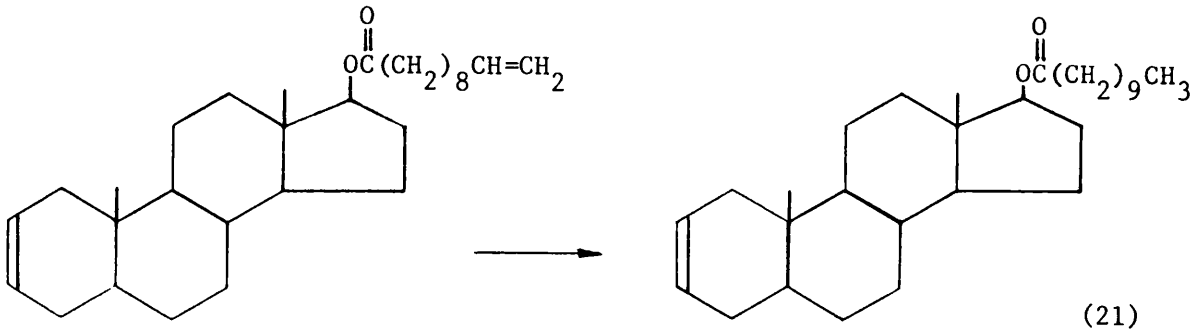
1.1.3. ADVANTAGES AND LIMITATIONS OF SUPPORTED CATALYSTS

The physical and chemical properties of inorganic compared to organic polymer anchored catalysts are sufficiently diverse to enable a wide range of catalytic reactions to be carried out, and this allows a catalyst system to be designed to perform a specific reaction under specific conditions.

A fundamental difference in the chemistry of a catalyst attached to a polymer or inorganic support is rigidity. Polymer supports having flexible ligand groups can chelate or multiply coordinate to metal centres, and this may result in catalyst deactivation. The rigid

structure of an inorganic supported catalyst can circumvent neighbouring intermolecular interaction, but to achieve this, anchored complexes must be distributed over a high surface area and the resulting catalyst concentration may be so slow that its practical utility is lost. Thus, control of the distribution of active centres in both support types although not easily achieved is extremely desirable in order to give active and stable systems. Supporting a complex often has a significant influence on catalytic activity, and product distributions differing from those of the soluble homogeneous analogue are frequently found. A prime example of catalyst enhancement is illustrated by Grubb's studies of supported titanocene.[69] The reduced titanocenes are very suseptible to dimerisation, but when anchored in very low concentrations (0.044 mmol of Ti per gram of polymer) on polystyrene and then subsequently reduced, the hydrogenation activity towards olefins increases 60 to 120 fold compared to the homogeneous system.

Changes in selectivity also often result on supporting catalysts. Thus, the internal double bond of the steroid shown below is reduced on using a homogeneous rhodium catalyst,[10] but by using a cross-linked supported rhodium analogue, regioselective control is achieved and only the side chain double bond is hydrogenated.



(21)

Many transition-metal complexes have restricted solubilities in solvents, and for catalytic applications either dilute solutions or expensive solvents have to be used. This can be avoided with polymer bound catalysts since a high concentration of metal complex can be affixed to the support. Catalyst substrates employing organic polymers as a support matrix have an upper temperature limit approaching 160°C, this being the stability limit of macroreticular type resins. Inorganic anchored catalysts are limited by the thermal stability of the metal complex on the anchoring bond and not the support, and this is dependent on the conditionsused (oxidising or non-oxidising). From an engineering viewpoint, one important advantage of anchored catalysts over their homogeneous counterparts is their ability to maintain virtually any desired catalyst concentration during reaction, which generally allows direct control of the reaction rate. Also, polymer bound catalysts will remain active at concentrations where the analogous homogeneous catalyst precipitates from solution.

A unique application of inorganic supported systems is in bifunctional catalysis, where one of the catalyst functions is associated with the support. This is analogous to reforming or hydroisomerisation reactions which are heterogeneously catalysed, where the metal function acts as the hydrogenation component and the support facilitates acidic isomerisation. Working on these lines Pittman *et al*[70] have reported multistep catalysis of sequential reactions using different metals bound within the same polymer.

Another advantage of catalysts anchored to an inorganic oxide compared with a polymeric substrate is the superior control over diffusional factors for the former substrate. Under variable temperature and solution conditions, polymer swelling makes practical control of diffusional variables difficult, whereas for inorganic substrates diffusional changes can be assumed negligible for most reaction conditions. With known surface areas and pore distribution over a wide range of pore sizes, the optimum inorganic support can be used to minimise diffusional limitations for a given reaction or application.

Grafted catalysts resemble conventional heterogeneous catalysts more closely than homogeneous systems in view of the restricted mobility and closeness of the metal centre to the support surface. Although grafted catalysts may have superior resistance to metal leaching or catalyst deactivation compared to either inorganic anchored catalysts, they suffer from the disadvantage of having limited ability to change their stereochemistry and electronic environment at the metal centre.

All types of supported transition-metal catalysts will be potentially unstable under certain reaction conditions. Leaching of the metal entity from the support surface into the liquid phase is a frequent problem, and for use in a fixed bed reactor the overall result would be a loss in activity as the catalyst is removed from the reaction zone. The leaching mechanism from both inorganic or organic supports could involve the constant breaking and reforming of labile ligand-metal bonds. Alternatively the ligand itself may react and promote leaching. For example, oxidation of a phosphine ligand to a phosphine oxide could

produce a more labile phosphine oxide-metal complex, and leaching of metal from this complex could result as oxidation progresses. Immobilised transition-metal catalysts may also become unstable as a result of poisoning. In the case of inorganic-anchored and grafted catalysts, poisoning through physical blocking of active sites by adsorbed species can occur, but for polymer-anchored catalysts this is less likely as the metal centres are bound to isolated polymer strands which are lipophilic in nature and present in a mobile environment. Poisoning by metals and polar substances of inorganic surfaces can be diminished by conversion to a lipophilic surface, or by increasing the chain length within the anchoring ligand. Side-reactions on solid support surfaces are another potential problem and can be reduced by either increasing the catalyst concentration, or by reacting the surface hydroxyl groups with an agent capable of producing an organic lipophilic layer (e.g. silylation).

1.1.4 PHYSICOCHEMICAL CHARACTERISATION OF SUPPORTED CATALYSTS

One of the major difficulties found with conventional heterogeneous catalysts is their characterisation, and the problems posed with heterogenised systems are very similar. Whilst the majority of heterogenising procedures are carried out under relatively mild conditions, the essential physical properties (total specific surface area, pore structure and volume) of the resulting catalyst are generally assumed to be identical with those of the uncomplexed support, unless complete breakdown of polymeric materials is evident.

However, less clear is the characterisation of attached ligands and the chemical identity of supported complexes. For SLP catalysts some definition of the complex can be made since the active metal centre is essentially homogeneous in nature.

Information concerning the degree of functionalisation of a support and the extent of metallation is normally found from bulk properties, typically elemental analysis. Additional characterisation from molecular weight determinations[71,72] and measurement of displaced material (e.g. phosphines,[73] carbon monoxide, propene[12]) during the attachment step, generally reflects the average composition of the material only. Information on coordination and matrix effects are often found from suitable application of spectroscopic techniques such as infrared spectroscopy,[17,18,72,74] electron spin resonance,[75] nuclear magnetic resonance.[71,76,77] Extended X-ray Absorption Fine Structure (EXAFS),[78] X-ray microprobe analysis,[79,80] and Electron Spectroscopy for Chemical Analysis (ESCA). Most relevant to our studies are infrared and nuclear magnetic resonance spectroscopy. From literature reports, most studies have been on supported carbonyl complexes where structures of proposed hybrid catalysts are based on comparison with soluble models. Unfortunately, for inorganic oxides absorptions below 1500 cm^{-1} are frequently masked by the support itself, and for polystyrene aromatic skeletal absorptions between 800-600 cm^{-1} are a dominant feature. Nuclear magnetic resonance studies on various nucleii in linear polymer supports are limited only by the abundance of a given nucleus compared to the same nucleus contained as an integral component of the support matrix. From crosslinked supports there is the complication arising from the insolubility of resin

materials, However, modern Fourier Transform techniques can be used to overcome such problems.

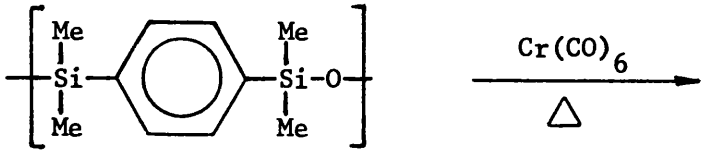
To date, mass spectrometry has received little attention as an analytical tool for studying supported catalysts. Coville and Nicolaides[81] have applied this technique to good effect in quantitatively measuring the degree of ring functionalisation in polystyrene polymers containing bromine, diphenylphosphine and the cyclopentadienyl moiety, prior to investigating a series of catalytic reactions.[82] However, their preliminary studies on transition metals supported on functionalised polymers have not revealed any fragments linked with the metal entity.

1.1.5 POLYSILOXANES AS A SUPPORT MATRIX

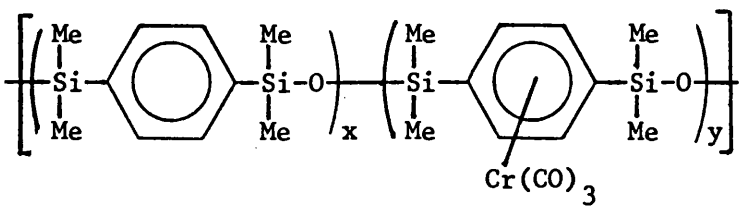
In view of the wide range of homogeneous catalysts and supports discussed so far, it is clear that the full potential of polymer and solid supported catalysts has yet to be revealed. Supported homogeneous catalysts frequently exhibit increased activity and/or selectivity for many catalytic applications, and research to date has focused primarily on crosslinked polystyrenes and silica supports with relatively few accounts of soluble polymer catalysts linked to liquid polymers such as poly(organosiloxanes). Of those studies published on polysiloxane supported transition-metal catalysts, little attempt has been made to accurately define the constitution of the catalytically active sites in the polymer matrix, or even the detailed structure of the polymer backbone in many instances. The relevant literature is reviewed in the next section.

In 1963, Brown[83] reported on the exceptional chemical, mechanical and thermal stability for 'ladder' polyphenylsilsesquioxanes, but it was not until 1975 that any reports appeared in the literature of transition-metal carbonyl entities bonded to the aryl rings of similar siloxane polymers.

Pittman et al[84] had previously prepared η^6-tricarbonylchromium complexed polystyrene by direct reaction of chromium hexacarbonyl with the polymer, and from polymerisation of styrenetricarbonyl-chromium where up to 40% of the aryl rings were metallated. The same authors[85] extended their studies to include polysiloxanes and prepared polytetramethyl-p-silphenylene-siloxane (I) and polymethylphenyl-siloxane (II) which on subsequent reaction with chromium hexacarbonyl generated η^6-$Cr(CO)_3$ complexed polysiloxanes with up to 19.3% metallation.



(I)



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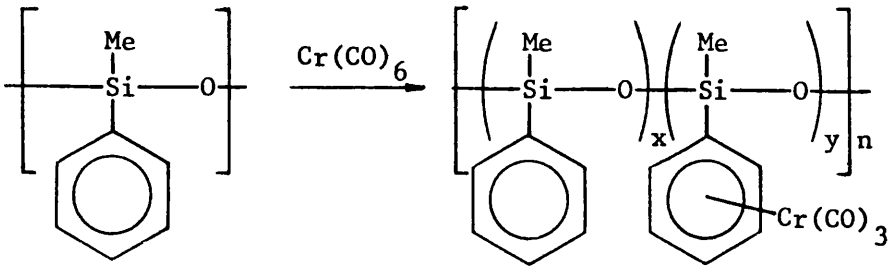


(23)

(II)

Awl et al[86] extended this approach by preparing a linear polyphenylsilsesquioxane and a ladder polyphenylsilsesquioxane, which, after thermal reaction with $Cr(CO)_6$ produced soluble stereoselective hydrogenation catalysts possessing very limited lifetimes owing to non-reversible dissociation of $Cr(CO)_3$ moieties.

Pittman[87] and co-workers subsequently prepared hydrolytically stable polysiloxanes incorporating the ferrocene moiety by polymerising 1,1'-bis(dimethylaminodimethylsilyl) ferrocene with aryl disilanols, but these compounds exhibited no catalytic activity.

A range of soluble (chlorosilyl)phosphine and siloxyphosphine complexes of rhodium(I) have been prepared by Brzezinska and Cullen.[88] The (chlorosilyl) and siloxyphosphines were prepared in good yields in the UV-induced reactions between diphenylphosphine and some vinyl- and octenylsilanes:

$$Ph_2PH + R'(R'')_2Si(CH_2)_nCH{=}CH_2 \longrightarrow R'(R'')_2Si(CH_2)_{n+2}PPh_2 \qquad (24)$$

n = 0, R' = R'' = Me

n = 0, R' = Me, R'' = Cl

n = 0, R' = Me, R'' = $OSiMe_3$

n = 0, R' = R'' = Cl

n = 6, R' = R'' = Cl

Polymeric siloxyphosphine rhodium(I) complexes were prepared[89] by hydrolysing in dioxane/water mixtures of preformed rhodium(I) complexes of the phosphines $Cl_3Si(CH_2)_nPPh_2$ (n = 2,8), either alone or in the presence of excess trichloromethylsilane, and although these metal-doped polymers possessed catalytic activity for the hydrogenation of alkenes, they were both ill-defined and non-reproducible[90].

$$\left[Cl_3Si(CH_2)_nPPh_2\right]_3RhCl + mCH_3SiCl_3 \xrightarrow{H_2O} \left[O_{3/2}Si(CH_2)_nPPh_2\right]_3RhCl(O_{3/2}Si(CH_3)_3)_m$$

(n = 2,8. m = 0-200) (25)

$$\left[Cl_3Si(CH_2)_2PPh_2\right]_4Rh_2Cl_2 + mCH_3SiCl_3 \xrightarrow{H_2O} \left[O_{3/2}Si(CH_2)_2PPh_2\right]_4Rh_2Cl_2(O_{3/2}SiMe_3)_m$$

(m = 0-200) (26)

Marciniec et al[91] adopted a similar approach in preparing phosphinated polyalkylsilsesquioxane supports (V,VI) which on complexation with Wilkinson's complex produced active catalysts for the hydrosilylation of 1-hexene by triethoxysilane.

$\left[Ph_2P(CH_2)_2SiO_{3/2}\right]_x$ (V)

$\left[Ph_2P(CH_2)_3SiO_{3/2}\right]_x$ (VI)

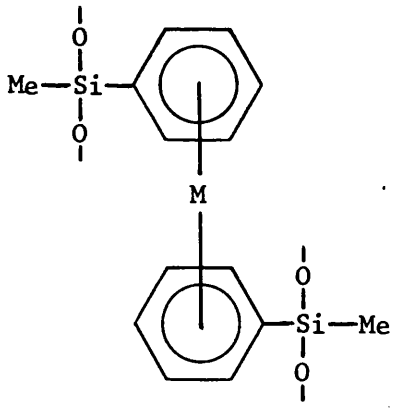
Conan et al[92] coated silica an organosilicon ladder polymer previously chloromethylated and phosphinated to yield a support which after reaction with Cramer's complex $\left[RhCl(C_2H_4)_2\right]_2$ afforded a hydrogenation catalyst. The authors report their catalyst had superior activity towards the hydrogenation of 1-hexene, cyclohexene and ∝-pinene than its homogeneous analogue by about a factor of 50, and several hundred times more active than other supported hydrogenation catalysts. In a further publication, Bartholin et al[93] prepared and examined several simple "model complexes" based on phosphine functionalised octaphenylsilsesquioxane and compared their catalytic activity with the above silica coated and true polymeric catalysts derived from phosphinated polyphenylsilsesquioxane. Their results showed that the silica coated catalyst was superior, and the authors[94] proposed that the exceptional activity originates from a change in the anchored rhodium species on reduction with hydrogen. This reduction is reported to occur for rhodium carbonyl compounds only.[94]

A polysiloxane support of unknown composition was used by Sanger and Schallig[95] to anchor $RhH(CO)_2(PPh_3)_2$ and so form an active hydroformylation catalyst. The starting material methyltriphenylsilicone polymer, was

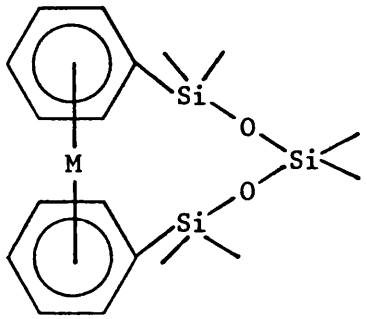
chloromethlated and subsequently phosphinated with $KPPh_2$ to give $\equiv SiC_6H_4CH_2PPh_2$ anchor sites which were used to fix rhodium complexes.

A series of iron tetracarbonyl π-complexes of vinylsilanes and a number of simple vinylsiloxanes have been prepared by Russian workers,[96] but these compounds were found to be very air sensitive and consequently of little value in catalysis.

More recently, Francis and Timms[97,98] synthesised thermally stable bis(π-arene) metal complexes (M = Ti, V, Cr, Mo) by metal atom condensation with poly(methylphenylsiloxanes) to give fluid metal bearing polymers.



(VII)



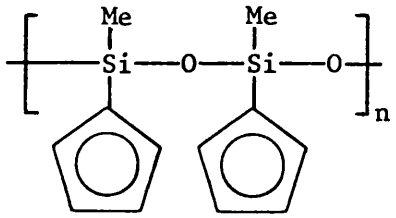
(VIII)

The coordination mode of metal atoms to the phenyl residues was either inter(VII) or intramolecular(VIII). Further work by Francis et al[99,100] extended this approach to organometallic polymers containing mononuclear and cluster metal sites randomly distributed throughout the polymeric structure, but no synthetic uses of these materials were noted.

Farrel et al[101] have prepared and tested the catalytic hydroformylation activity of halocarbonylrhodium(I) complexes containing

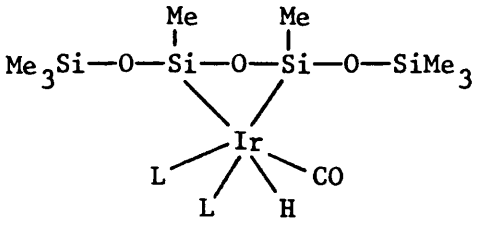
phosphinoalkylorganosilicon ligands. Only one example of a siloxane was included in their studies, $\left[Ph_2PCH_2(Me)Si(OSiMe_2)_3O\right]$, which readily formed a polymer anchored complex with $\left[Rh(CO)_2Cl\right]_2$.

In a 1983 publication, Curtis et al[102] reported the preparation of titanocene anchored derivatives of tetramethyldisiloxane and poly-(methylsiloxane). The latter species (although not tested for any catalytic activity) can be considered an analogous counterpart to organic polymer and silica supported titanocene derivatives prepared by Grubb's et al,[69] and Jackson's group[103] respectively. The synthesis involved chlorination of poly(methylsiloxane) followed by reaction with sodium cyclopentadienide to generate the poly(cyclopentadienylmethylsiloxane) (IX). Following reaction with sodium metal or n-butyllithium, the anionic cyclopentadienide derivative was reacted with $TiCl_4.2py$ to yield $\left[1,1'-\eta^5,\eta^5-(Me_2Si_2O_2)(C_5H_4)_2TiCl_2\right]_n$.



(IX)

Although not synthesised for any catalytic application, Gustavson[104] and co-workers prepared a novel cycloiridiadisiloxane through reaction of Vaska's complex $(Ph_3P)_2Ir(CO)Cl$ with 1,1,1,3,5,7,7,7,-octamethyl-tetrasiloxane.



(27)

(L = PPh_3)

Only a few reports of other transition-metal entities being incorporated into silicon polymers are available. Adrianov[105] condensed titanocene dichloride with disodium salts of disilanols to produce macromolocules having Ti-O-Si linkages, and Avilova, Bykov and Kondratenko[106] have reported siloxane polymers with Si-O-Cr links, but with ill-defined structures.

Thus several isolated and fragmentary reports on the chemical properties of metallated polysiloxanes have been published, but systematic and careful studies of the catalytic potential of this novel class of compound remain to be carried out.

1.2 SILOXANES

1.2.1 GENERAL CONSIDERATIONS ON ORGANOSILOXANES

In general terms, silicones may be defined as organosilicon polymers having silicon atoms bound to each other through oxygen atom links, with the silicon valencies not associated with oxygen being saturated by organic groups. Silicones is a name now given to commercial products such as rubbers, resins, oils and salt like compounds, whereas the term siloxane is used in scientific terminology.

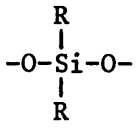
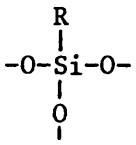
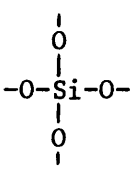
Silicones have been characterised according to their general structural principles, i.e.

i) Silicones are polymeric and have many of the structural characteristics of organic polymers,

ii) They possess silicon-oxygen bonds and are fundamentally related to the structural units of silicates and silicic acids.

The silicon atoms in polyorganosiloxanes can be in combination with one, two or three organic groups, whilst the remaining valencies are satisfied by oxygen atoms. Thus, mono-, di-, tri- and tetrafunctional siloxane units form the basis of polysiloxanes with the latter unit $(SiO_4)^{4-}$ forming the structural unit for silicates and silica.

Table 1.3 Polyorganosiloxane structural units

Structural formula	Composition	Functionality	Symbol
R_3SiO-	$R_3SiO_{1/2}$	monofunctional	M
	$R_2SiO_{2/2}$	difunctional	D
	$RSiO_{3/2}$	trifunctional	T
	$SiO_{4/2}$	tetrafunctional	Q

The symbols M,D,T and Q have been used to good effect in representing quickly and clearly the structures of high molecular weight complex polymers. In analogy with organic polymers, siloxane polymers can be distinguished according to their structures:

i) Linear polysiloxanes corresponding to the structural type MD_nM. Oligomeric polysiloxanes having definite low molecular weights which can be isolated by crystallisation or distillation may be prepared by insertion of difunctional units to give siloxanes of formula

$$R_3SiO\left[R_2SiO\right]_nSiR_3$$

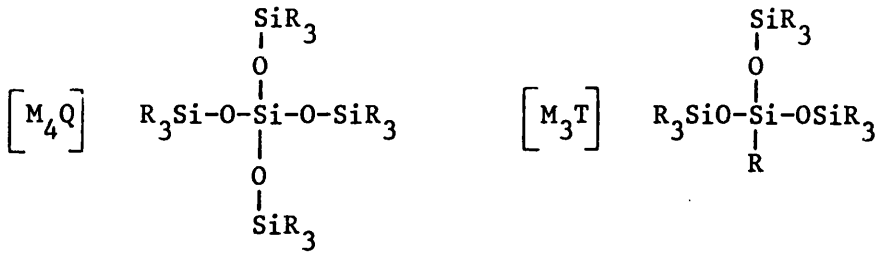
The lowest member has n = 0, hence giving a hexaorganodisiloxane

$$R_3SiOSiR_3 \left[M_2\right]$$

The nature of the organic substituents R largely determines the physicochemical behaviour of linear polyorganosiloxanes of comparable molecular weights since only weak intermolecular forces act between siloxane chains. High molecular weight polymers with lower aliphatic groups (R = Me) are viscous liquids at room temperature, but analogous aromatically substituted siloxanes are solids, e.g, hexaphenyldisiloxane m.p. 226°C. Modification of linear polysiloxanes can be achieved by insertion of silicon-functional and/or organofunctional atoms in the chain, or by variation of organic substituents on silicon atoms. There may be differences in reactivity between functional groups substituted in D or M units, and those substituted in monomers. This can be attributed to such effects as steric factors, molecular coiling or inductive effects, possibly through neighbouring siloxane linkages.

ii) Branched-chain polysiloxanes which contain a minimum of one trifunctional (T) or tetrafunctional (Q) siloxane unit serving as a centre of branching within a chain or ring. Only a few examples of

oligomeric organosiloxanes of defined structure are known where branching effects on physicochemical behaviour can be studied.



iii) Cyclic polysiloxanes which are composed of siloxane rings. Monocyclic molecules consisting of difunctional siloxane units are characterised by the symbol D_n. Condensed ring systems are called polycyclic, and contain T units which link groups between rings. Spirocyclic systems have Q units at the point of linkage, which distinguishes them from polycyclic systems as a separate group. From the tetrahedral coordination of oxygen atoms around a silicon atom in a Q unit, the alternate ring planes are sited perpendicular to one another. A further subgroup of cyclic polymers are termed spherocyclic, and are built up from a number of rings giving a molecule consisting only of T groups.

iv) Cross-linked polymers are two or three dimensional networks of linear or cyclic molecules that have been cross-linked by T or Q units.

1.2.2. SYNTHETIC METHODS

There are numerous methods available for synthesising poly(organosiloxanes) from monomeric silicon functional organosilanes.[107] By virtue of simplicity and economy, the most frequently used process involves

hydrolysis. Other methods which are only partially dependent on hydrolysis use alcohols, alkoxysilanes, inorganic oxides and silanols etc. as the source of oxygen for siloxane bond formation.

The hydrolysis reaction initially leads to silanols, but in view of the instability of the silanol bond, condensation frequently takes place spontaneously to yield polymeric siloxanes. The structural siloxane units M, D, T and Q outlined previously are obtained from functionalised silanes accordingly:

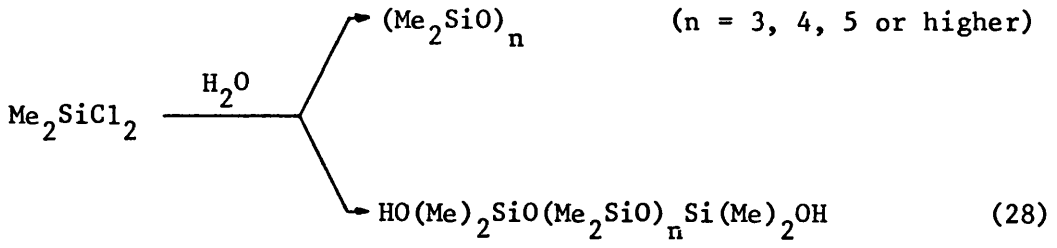
Silane	Silanol intermediate	Siloxane unit
R_3SiX	$R_3Si(OH)$	$R_3SiO_{1/2}$
R_2SiX_2	$R_2Si(OH)_2$	$R_2SiO_{2/2}$
$RSiX_3$	$RSi(OH)_3$	$RSiO_{3/2}$
SiX_4	$Si(OH)_4$	$SiO_{4/2}$

When mixtures of silanes having different functionalities are hydrolysed, the method used has significant influence on the resultant siloxane with respect to size and structure. The final structure is obtained as a result of the last condensation reaction. The rate of hydrolysis is influenced by the components used, and increases with polarity of the Si-X bond and on the number of X atoms or groups bonded to silicon in each molecule. The rate is also affected by the size, number and type of organic groups present, since ease of nucleophilic attack by water molecules and hence scission of the Si-X bond will be diminished with increasing steric hindrance. If electronegative effects are dominant, the Si-X bond strength increases and reactivity to nucleophiles is

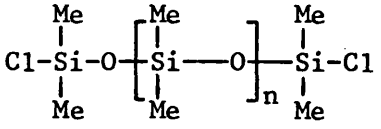
lessened. Thus, phenyl substituted chlorosilanes hydrolyse at a slower rate compared to their analogous methylchlorosilane counterparts. Another consideration that may affect hydrolysis is the characteristics of the Si-C bond. An Si-C bond is weakly polar, and will be sensitive to acids formed during halosilane hydrolysis than normal C-C bonds.

When all these factors have been considered, the method used must facilitate hydrolysis and condensation to a copolymer. If the components of a siloxane mixture have different inclinations to both hydrolysis and self-condensation, then a simultaneous cocondensation with hydrolysis may not readily occur.

The hydrolysis reaction essentially consists of mixing one or more organohalosilanes with excess water and judging the dilution accordingly to prevent strong hydrochloric acid ($<20\%$) from being formed, although this can accelerate the self-condensation of silanols. The exothermic reaction is usually cooled owing to the heat evolved by dissolution of hydrogen chloride in water. Organic solvents, typically toluene, diethyl ether and dibutyl ether, which are either immiscible or slightly miscible with water, and yet show no reactivity toward the halosilane, are often used for dilution, product distribution and separation purposes, since the hydrolysis products are taken up by the solvent and are protected from attack by the strong aqueous acid generated in situ. Dilution of the siloxane phase will promote intramolecular over intermolecular condensation, and when difunctional silanes such as dimethyldichlorosilane are used low polycyclosiloxanes are formed preferentially. However, when dimethyldichlorosilane is hydrolysed in water alone, a mixture of linear siloxanediols and cyclosiloxanes are produced, i.e.



On hydrolysis with water in an inert water-miscible solvent (e.g. dioxane) low molecular weight polycyclosiloxanes are formed in high yield. Hydrolysis reactions of di- and trichlorosilanes using an excess of water in an organic solvent can promote formation of polysiloxane products having silanol groups in abundance, whereas for reactions in which the number of moles of chlorosilane are greater than those of water, polysiloxanes with terminal chlorine atoms (X) are formed, i.e.



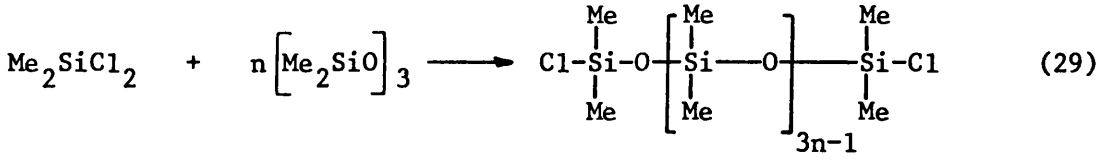
(X)

By varying the acid concentration in solution, different product ratios can result since the acid, for example sulphuric acid, can function as a catalyst and so facilitate formation of high molecular weight polysiloxanes.

As well as hydrolytic methods of preparing polysiloxanes, other polymerisation procedures utilising thermal, acid-, and base catalysis to convert low molecular weight polyorganosiloxanes into high molecular weight products are known.

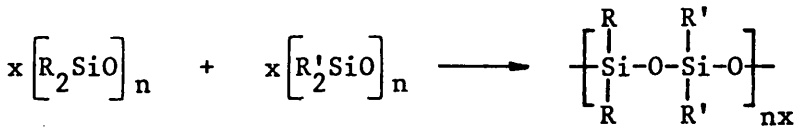
Low molecular weight cyclic polydiorganosiloxanes can rearrange to give

high molecular weight polymers when heated to 250 - 300°C in a closed system. Temperature limits are governed by the cleavage sensitivity of the Si-C bond and on the susceptibility of the organic groups to thermal decomposition. By increasing temperature and pressure, the yields of high molecular weight products are raised. If dual siloxane systems such as polydiorganocyclosiloxane and dimethyldichlorosilane are heated in a closed system, then telomerisation and ring opening can give the following type of product.



(29)

Two organosiloxanes having different substituents and molecular weights can be copolymerised to form a high molecular weight polysiloxane having a guassian molecular weight distribution curve with a single maxima.



(30)

This process involves equilibriation of the mixture of polysiloxanes so that cleavage and re-forming of siloxane bonds occurs so bringing the system to a state of maximum thermodynamic stability. Acids and bases are frequently employed as catalysts to accelerate this process and to moderate the reaction conditions, but their possible interaction with organic groups must also be considered. When siloxane bonds are cleaved, the high energy intermediate complexes so formed, spontaneously change

to yield low energy polymers, and for every decrease in size of the larger siloxane molecules there is a simultaneous increase in the size of the smaller molecules.

The initial step in an acid catalysed polymerisation reaction involves attachment of a proton to the oxygen atom of a siloxane bond to form an oxonium complex. This complex is unstable and is suseptible to nucleophilic attack. On decomposing through cleavage of the Si-O link, Si-OH and Si-X bonds react further to regenerate the acid and form a new siloxane linkage. A series of bond scissions and reformations follow to form a polysiloxane chain as a result of a favourable energy gradient, i.e.

$$\equiv Si\text{-}O\text{-}Si\equiv + H^+ \longrightarrow \equiv Si\text{-}\overset{+}{O}(H)\text{-}Si\equiv$$

$$\equiv Si\text{-}\overset{+}{O}(H)\text{-}Si\equiv + X^- \longrightarrow \equiv Si\text{-}OH + X\text{-}Si\equiv$$

$$\equiv Si\text{-}OH + X\text{-}Si\equiv \longrightarrow \equiv Si\text{-}O\text{-}Si\equiv + HX \qquad (31)$$

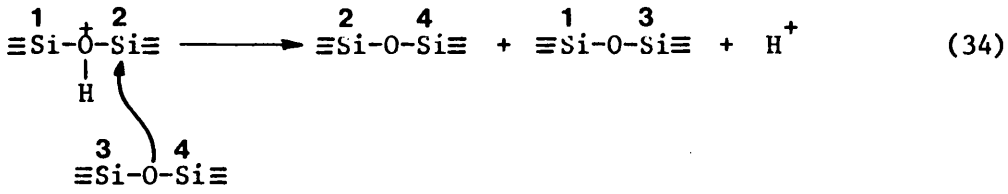
Alternatively, two silanol groupings may condense to form a new siloxane linkage with the elimination of water which can promote further silanol group production through hydrolysis of an Si-X bond, i.e.

$$\equiv Si\text{-}OH + HO\text{-}Si\equiv \longrightarrow \equiv Si\text{-}O\text{-}Si\equiv + H_2O \qquad (32)$$

$$\equiv Si\text{-}X + H_2O \longrightarrow \equiv Si\text{-}OH + HX \qquad (33)$$

Another mechanism may occur which involves nucleophilic attack on the oxonium complex by a siloxane oxygen of an unprotonised molecule to form

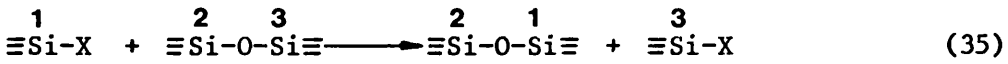
a new siloxane linkage, i.e.



(34)

Sulphuric, ethylsulphuric, chlorosulphonic, nitric and phosphoric acids are frequently used as catalysts.

Acid equilibriation of polysiloxanes with organohalosilanes proceeds by an exchange reaction where the silicon atoms of the halosilane become incorporated into the siloxane chain, i.e.



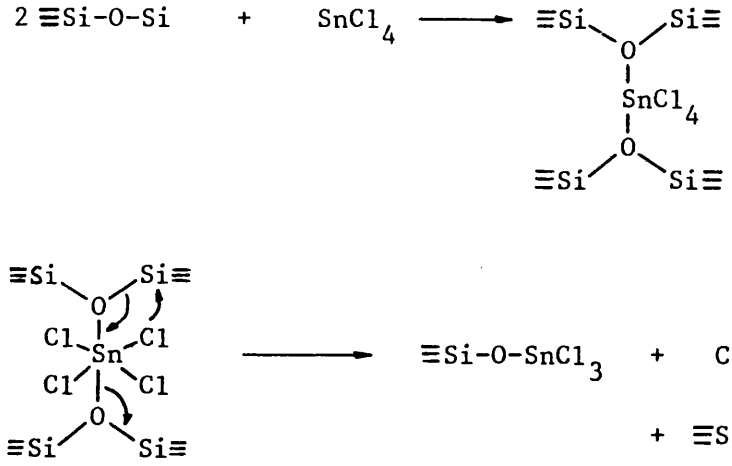
(35)

Hydrochloric acid or iron(III) chloride hexahydrate are known to catalyse this reaction.

The nature of the organic groups or their substituents strongly influence the reactivity of the Si-O-Si bond in acid catalysis. Increasing the size of the aliphatic substituent decreases the reactivity; thus methyl-siloxanes are easier to equilibriate and polymerise than aromatic siloxanes. Similarly, substituents in functionalised organosiloxanes that are electron acceptors will decrease reactivity to acid catalysis.

On completion of polymerisation, catalyst removal is generally necessary to prevent any subsequent affect on the polymers heat aging properties. This can be achieved by washing with water or by neutralisation. For the former, homogenisers are frequently used, or alternatively the polymer is stirred after dissolution in a water-immiscible organic solvent, and then simple phase separation is effected. This latter technique can be employed if the salts formed from a base neutralisation cannot be removed

by filtration. Lewis acids of the Friedel Crafts type are known to cleave siloxane links, and if the reactions involved are reversible then siloxane bond redistribution will occur, e.g.



(36)

This mechanism is similar to that of a protic acid, where an oxygen atom of the siloxane initially acts as an electron donor towards the catalyst. The key feature here is the instability of the adduct formed between the siloxane and Lewis acid which decomposes to regenerate the catalyst and a new Si-O bond.

Polymerisation by alkaline catalysts proceeds by formation of a high energy activated intermediate at the siloxane linkage which decomposes to give moieties which through condensation reactions form new Si-O-Si bonds. As with acid catalysis, the alkaline catalyst promotes cleavage and rearrangement of siloxane bonds leading to polymer formation. The initial reaction of KOH catalysts is attachment of the base to the silicon atom:

$$\equiv Si\text{-}O\text{-}Si\equiv \xrightarrow{OH^-} \equiv Si\text{-}O\text{-}\underset{\underset{OH}{|}}{\bar{S}i}\equiv$$

$$\equiv Si\text{-}O\text{-}\underset{\underset{OH}{|}}{\bar{S}i}\equiv \longrightarrow \equiv Si\text{-}O^- + HO\text{-}Si\equiv$$

$$\equiv Si\text{-}O^- + HO\text{-}Si\equiv + K^+ \longrightarrow \equiv Si\text{-}OK + HO\text{-}Si\equiv$$

$$\equiv Si\text{-}OK + HO\text{-}Si\equiv \longrightarrow \equiv Si\text{-}O\text{-}Si\equiv + KOH \qquad (37)$$

As for acid catalysis, the choice of solvent can influence the rate of rearrangement. Thus, increasing the polarity of the solvent results in the formation of a high concentration of $Si\text{-}\bar{O}$ ions, and a fast attainment of equilibrium.

Alkaline catalysts can be removed by the methods described for acid catalysis.

1.2.3. PROPERTIES AND USES OF COMMERCIAL SILOXANES

Polysiloxanes have high thermal and chemical stability, and a good resistance to moisture, sunlight, oxygen and ozone. Structure and composition determine the technical properties of polysiloxanes and related organosilanes, with the nature of the siloxane bond being an important factor for the former class of compound.

The siloxane bond is formed from σ- coupling of hybridised s- and p- electrons of a silicon atom with oxygen p- electrons. A π- interaction between unshared oxygen p- electrons and 3d orbitals of silicon to form p_π-d_π coupling[108] is also possible. The majority of organosiloxane

compounds have an Si-O bond length of 1.64 ± 0.03Å. The SiOSi bond angle varies from 105°- 170° with a high proportion in the 130°- 150° range.[108] In contrast, the OSiO bond angle has narrower limits, namely 110°- 120°. The siloxane bond is very stable, and bond strengths calculated from heats of combustion measurements range from 420-490 kJ $mol.^{-1}$

A few notable physical properties which are characteristic of polydimethyl and structurally similar siloxanes are low surface tensions due to weak intermolecular interactions, and high compressibility, and this property shows a tendency to decrease with increasing molecular weight. These polymers also exhibit minimal viscosity change with change in temperature compared to other polymer types. Polydimethylsiloxanes are mobile at low temperatures although very high molecular weight samples ($\cdot 10^6$ daltons) which are considered to be elastomers tend to be solids. The thermal stability of these materials is well known, but samples must be free from acid or base impurities after their preparation to reduce siloxane bond rupture. Generally, thermal degradation of high molecular weight samples begins above 500K and becomes pronounced at 650 - 700K.

Two other classes of siloxanes which are of importance are branched and ladder polymers composed of trifunctional (T) units. These are polyorganosilsesquioxanes of general formula $(RSiO_3)_n$ with polyphenyl-silsesquioxane $(PhSiO_3)_n$ being a notable member. Besides a high thermal stability, this polymer has excellent solubility in organic solvents and good corrosion inertness.

Silicones are well known for their stability when subject to heat, radiation and chemical attack, and applications in oil seals, nuclear reactor seals,paints and roof coatings take advantage of this stability. However, there are other properties that must be considered. With addition

of fillers and other additives, the mechanical properties of silicones can be refined to meet a wide variety of applications. Materials which have been used in engineering have often contained a second phase such as amorphous silica to give increased strength. Interaction of silica with a silicone polymer increases the degree of cross-linking, and permits energy to be dissipated during mechanical deformation.

When fillers are present the rheological properties are often altered, for example, the viscosity of a silicone fluid will now increase and the deviation from Newtonian behaviour will become greater. Applications of these fluids are based on stability and high polymer chain flexibility, e.g. brake fluids using viscosity-temperature relations, and liquid springs using compressibility properties.

A large number of polysiloxanes act as good insulators, and their surface hydrophobic character aids in repelling water to assure retention of insulating properties. The nature of side groups will affect electrical properties, with polar substituents decreasing resistivity and increasing the dielectric constant. However, when fillers are present, no significant changes in insulating properties are found. Silicone elastomers containing carbon black have found good use as spark plug boots and wire cores, and even on complete thermal degragradation the oxidation product is a non-conducting SiO_2 ash, Other uses of silicones with resistivity properties are in capacitor and transformer fluids, and high temperature water insulators.

Commercial elastomers, fluids and resins find many applications from their transparency and permeability properties. Dimethylsiloxane polymers have a high transmittance of light over a broad range of wavelengths, often greater than other silicone elastomers. Permeability is dependent on

diffusivity and solubility, and when comparing silicones with other common polymers it is the former that have highest permeability values. Their oxygen permeability of polydimethylsiloxanes is not too dependent on the degree of cross-linking or the amount of filler present in the polymer, and applications in contact lenses, blood oxygenators, solar stills and fabric coatings have resulted.

The biological inertness of polydimethylsiloxane fluids, gels and elastomers give rise to their use in food processing, personal care products and prosthetic devices such as finger joints and breast implants. In all applications there is an important emphasis placed on the inertness and chemical/physical stability of the elastomer in the physiological environment. The interaction of soil with polydimethylsiloxane promotes hydrolysis and rearrangement to give an equilibrium mixture of dimethyl cyclics and silanol end-blocked linear polymers. Besides inert polydimethylsiloxanes, other silicon containing compounds exhibit biological activities which are a function of size, configuration and silicon substituents, e.g. trimethylsilanol is a central nervous system depressant. These bioactivities are not always predictable from structure reactivity considerations, and silicon-containing compounds should always be treated with respect.

1.3. APPLICATIONS OF SUPPORTED CATALYSTS

The reactions, principally of olefinic substrates, that have been studied and catalysed by supported complexes include hydrogenation, hydrosilylation, hydroformylation, oxidative hydrolysis, acetoxylation and carbonylation. Some of these reactions will now be discussed in more detail.

1.3.1. HYDROGENATION

A large number of systems have been studied as hydrogenation catalysts with the majority utilising d^8- metal complexes of rhodium(I), palladium(II) and platinum(II). To receive maximum efficiency from a catalyst for a particular hydrogenation reaction, a number of parameters can be varied. Firstly, the nature of the support will be considered. For the hydrogenation of cyclic olefins, phosphinated silica has frequently been found to exhibit greater activity than phosphinated polystyrene or polyvinylchloride supports. This may be attributable to an easier access of substrates to rhodium(I) complexes bound to the exterior of the silica surface compared to functionalised polystyrene where the active sites may be located in the interior of polymer beads. However, this effect can be of value in selectively hydrogenating one olefin component of a mixture.

Cross-linking in a polymer support can have a profound affect on the catalytic activity of a catalyst. Increasing the degree of cross-linking generally decreases activity, but often increases the specificity since the polymer chains are bound tightly together and so entry to the interior will be restricted to small substrate molecules only. For example, using 2% cross-linked polystyrene the following rates of hydrogenation in benzene for a range of olefins decreased in the order:

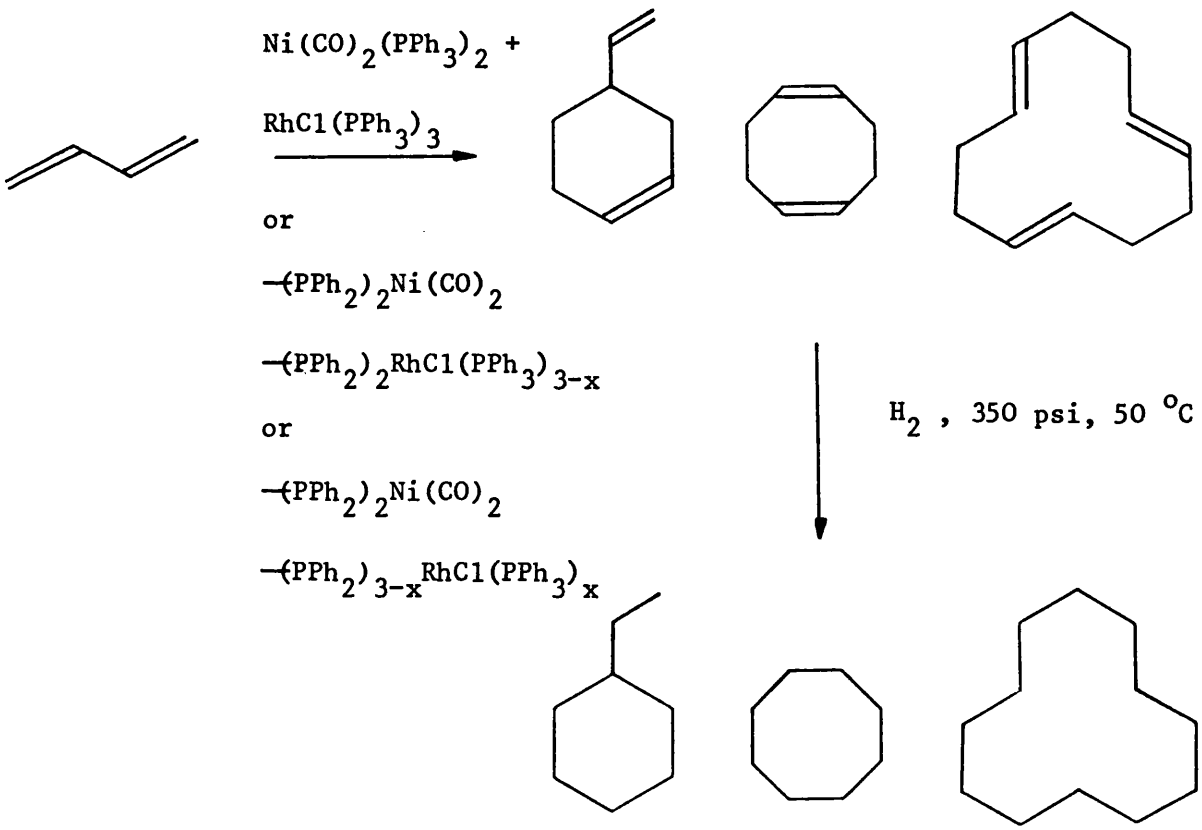
$$\text{1-hexene} \gg \text{cyclohexene} \gg \text{cyclooctene} > \text{cyclododecene}$$

Grubbs[109] and Pittman[110] have attempted to synthesise active polystyrene supported analogues of Wilkinson's catalyst. Grubbs used large beads of a 2% cross-linked polymer which resulted in a catalyst 0.06 times as active as the homogeneous counterpart. Pittman achieved an activity factor of 0.8 for small beads of a 1% cross-linked polymer.

Two further factors to consider are the nature of the metal complex and the solvent used. For polystyrene, increasing the solvent polarity will cause a decrease in polymer swelling, but this can be varied to give control of activity and selectivity of a designated supported catalyst. With all factors being equal, the activity of rhodium(I) complexes supported on phosphine functionalised polystyrene decreases in the order,

$RhCl_3 > RhCl_3 + PPh_3 > RhCl_3 + HPPh_2 > RhCl_3 + C_2H_4 > RhCl(PPh_3)_3$

Pittman and Smith,[70] in a 1975 publication, demonstrated sequential multistep reactions using rhodium catalysts in conjunction with nickel catalysts and unique rhodium-nickel catalysts supported on phosphine functionalised styrene-divinylbenzene resins for the cyclooligomerisation and hydrogenation of butadiene. These catalysed reactions can be represented by the following sequence using any of the catalyst combinations shown:



(38)

Pittman found that equivalent results could be obtained for both homogeneous catalysts, mixtures of the appropriate anchored catalysts, and the unique mixed species having rhodium and nickel on the same supports. In comparison to the rate of hydrogenation found for $RhCl(PPh_3)_3$, the mixture of separately anchored catalysts was about 0.8 times as fast, whereas the combined metal catalyst was only 0.15 times as active. Although the rates are different, Pittman's studies show that homogeneous catalysts can be duplicated by supported analogues which often have a number of advantages.

The British Petroleum group of workers[55] have prepared three types of hydrogenation catalyst using phosphine functionalised silica

$$SIL\text{—}\left(\text{—}CH_2\right)_2PPh_2\Big]_3RhCl \qquad \text{(XI)}$$

$$SIL\text{—}\left(\text{—}CH_2\right)_2PPh_2\Big]_2RhBr \qquad \text{(XII)}$$

$$SIL\text{—}\left(\text{—}CH_2\right)_2P(n\text{-}C_6H_{13})_2\Big]_2RhCl \qquad \text{(XIII)}$$

All three could be used under continuous flow conditions to hydrogenate isoprene, 1-hexene and cyclohexene, and in the presence of n-butyl mercaptan no significant poisoning was observed. Of the three catalysts, only the cyclohexylphosphine derivative gave consistent results over extended use.

The Czechoslovakian workers Czaková and Capka[111] synthesised a range of phosphine functionalised silica supported rhodium hydrogenation catalysts. The silylphosphine ligands, prior to attachment to silica, can be represented by:

$(EtO)_3Si(CH_2)_nPPh_2$ (n = 4-6) (XIV)

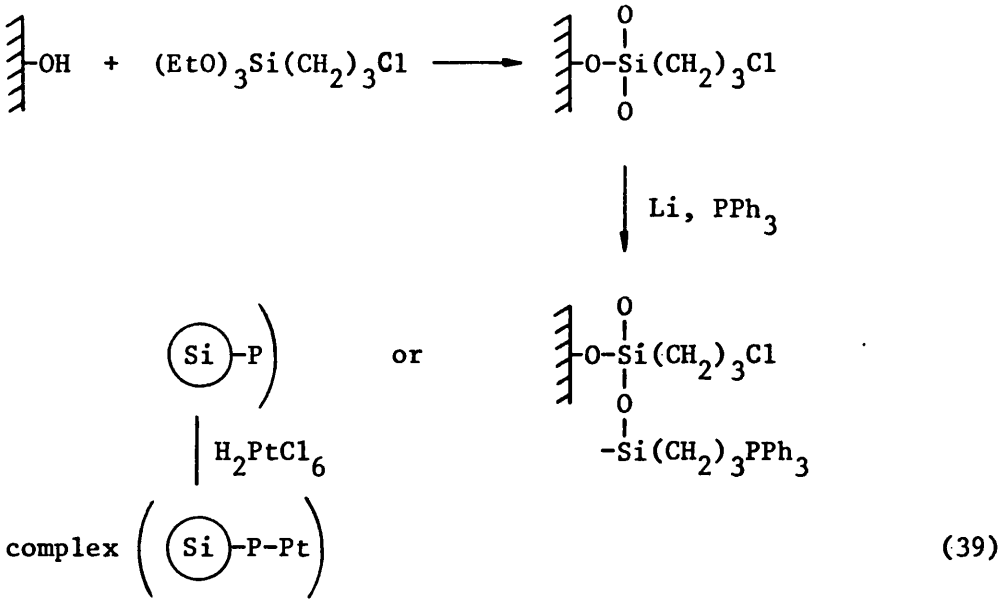
$(EtO)_mSi(CH_2)_{3-m}SiCH_2PPh_2$ (m = 1-3) (XV)

From a series of olefin hydrogenation reactions, the most efficient catalysts were found to be those with a short spacer-chain separating the diphenylphosphino group from the silica surface. This restricts the mobility of a rhodium atom and so helps prevent deactivation through interaction with the surface. Czakovà and Capka also compared the activity of catalysts anchored to silica through ligands containing the same methylene chain but differing in the number of ethoxy groups on silicon, and established that the use of diethoxymethylsilyl substituted phosphine in place of a triethoxysilyl substituted ligand does not affect catalytic activity, but is only influenced by spacer-chain length. This is in contrast to studies made by Brzezinska et al[90] who found that by increasing the spacer arm (n) between the metal and polymer matrix in siloxyphosphine rhodium(I) complexes of idealised formula

$$\left[O_{3/2}Si(CH_2)_nPPh_2\right]_3RhCl(O_{3/2}SiCH_3)_m \quad (n = 2\text{-}8,\ m = 0\text{-}200) \quad (XVI)$$

gave hydrogenation catalysts which maintained their activity in benzene at 25°C over a number of cycles. The authors presumed that a longer spacer arm would inhibit dimer formation and probably allow the active sites to behave more like species in solution.

A similar phosphine functionalised silica has been utilised by Chinese workers[112] in preparing a supported poly-γ-diphenylphosphinopropylsiloxane platinum complex which serves as an active catalyst.



(39)

However, for the hydrogenation of benzene the presence of hydrochloric acid is necessary for complete reaction. The reduction results for toluene are similar to those of benzene, but the product must be separated immediately to avoid conversion into isoheptane.

In a comparism to Grubbs polystyrene supported titanocene derivative,[69] Jackson et al[103] reported a silica anchored analogue. The authors found the silica supported titanium catalysts to have superior activity compared to the homogeneous "titanocene" complex for the reduction of terminal olefins, but similar rates were found for the hydrogenation of internal olefins. However, whereas the homogeneous catalyst lost activity through dimerising, the supported complexes gave constant reduction rates which is in contrast to that reported by Grubbs et al for hydrogenation using polymer supported catalysts, where increased rates were observed.

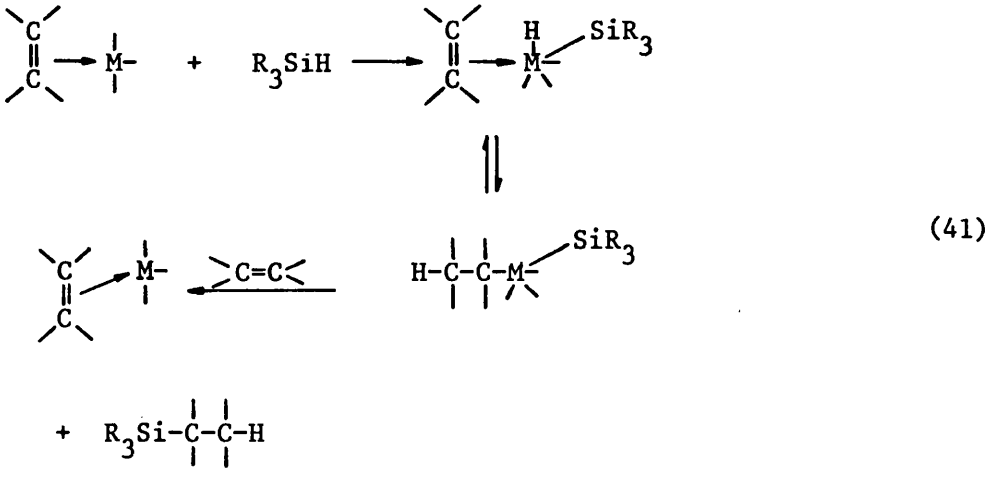
1.3.2 HYDROSILYLATION

A hydrosilylation reaction is essentially the addition of an R_3Si unit and a hydrogen atom to an organic compound possessing an unsaturated group, typically olefins, acetylene or ketones.

$$R_3SiH + R'CH{=}CH_2 \xrightarrow{\text{catalyst}} \begin{cases} \rightarrow R'CH_2CH_2SiR_3 \\ \rightarrow CH_3CHR'SiR_3 \end{cases} \qquad (40)$$

(where R may be halide, alkyl, alkoxy)

For the homogeneously catalysed reaction, the principal catalysts used have contained rhodium or platinum, for example Wilkinson's complex and chloroplatinic acid, H_2PtCl_6, respectively. The hydrosilylation mechanism is believed to involve oxidative addition of $H\text{-}SiR_3$ to give a rhodium(III) or platinum(IV) intermediate, which then facilitates a transfer of H and SiR_3 to the unsaturated bond, i.e.



(41)

This mechanism is presumed to occur for supported catalysts as well.

A hydrosilylation catalyst can function in three ways:

i) reaction could occur at the metal site which is bonded to and remains on the support during the reaction.

This mechanism is supported from the overall yields and selectivity found for recycling of polymer anchored catalysts in comparism to their homogeneous analogues. The selectivity of supported catalysts has been illustrated in the hydrosilylation of isobutyrophenone,[113] where reaction occurs in the pores of the catalyst with activity being determined from the rates of diffusion of reactants to the active site.

ii) the active metal entity or its precursor may participate in a reversible process where it is abstracted from the support into solution. This effectively makes the catalytic process homogeneous in nature, and activity will be dependent on the ease of abstraction of the active species from the support.

iii) as for mode (ii), but with an irreversible abstraction process. However, this is unlikely in view of slight increases in catalytic activity being found on catalyst recycling.

A complementary silane activity series for rhodium and platinum catalysts has been found. For rhodium, the order is $HSi(OEt)_3 > HSiEt_3 > HSiCl_3$, and for platinum $HSiCl_3 > HSi(OEt)_3 > HSiEt_3$, with these specificities being found for the analogous homogeneous catalysts.

Marciniec *et al*[114] have made some notable studies on supported metal complexes as hydrosilylation catalysts. In a 1981 publication, the authors reported the preparation of platinum and rhodium complexes bonded to silica via binary amines, e.g. diethylamine, diphenylamine, pyrrolidine, and found these to be effective in various C=C hydrosilylation reactions for the preparation of organosilicon monomers and coupling agents.

The anchoring of tertiary amines to silica can be represented by the following equations:

$$SIL + Cl_3Si(CH_2)_3Cl \longrightarrow SIL\text{-}Si(CH_2)_3Cl$$

$$SIL\text{-}Si(CH_2)_3Cl + R_2NH \longrightarrow SIL\text{-}Si(CH_2)_3NR_2 \qquad (42)$$

The authors generally found no dramatic changes in hydrosilylation activity for different amines linked to silica, and only small activity differences were seen for differing quantities of amine silyl ligand anchored and for varying amine-metal ratios.

A further study by Marciniec et al[91] was to evaluate the role of phosphine functionalised polymeric organosilicon supports anchoring rhodium complexes for the hydrosilylation of C=C bonds. A number of silylphosphine and polysiloxyalkylphosphines which cause modification of Wilkinson's catalyst were prepared, i.e.

$$\left[Ph_2P(CH_2)_xSi(OEt)_3\right]RhCl \qquad \text{and} \qquad \left[O_{3/2}Si(CH_2)_xPPh_2\right]_yRhCl(PPh_3)_n$$

(XVII) (XVIII)

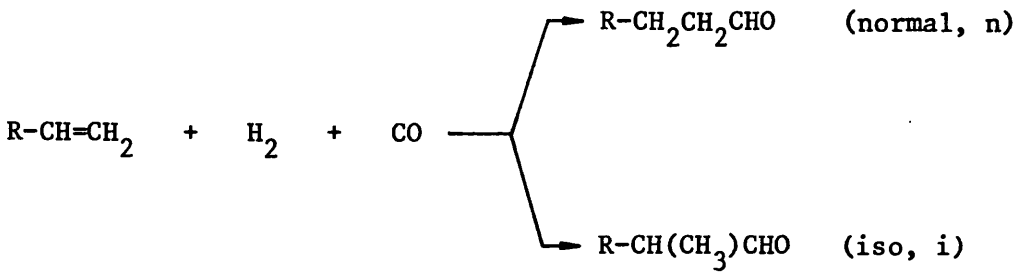
respectively, where x = 2 or 3.

All catalysts and Wilkinson's complex were tested in the hydrosilylation of 1-hexene by triethoxysilane. Their results essentially show no effect from the silylphosphine ligands on the reactivity of soluble Wilkinson-type catalysts for hydrosilylation, but the polymeric siloxane supports gave different yields of adducts (89 and 69%) compared to Wilkinson's complex (74%) at a reaction temperature of 80°C. From kinetic measurements, both supported catalysts show the same activity as Wilkinson's complex, whereas the homogeneous silylphosphine complexes have inferior activity towards the hydrosilylation of 1-hexene.

This is presumed to be due to the electronegative character of ethoxy groups on silicon which reduces the basicity of siloxyphosphine ligands compared to triphenylphosphine groups of Wilkinson's catalyst.

1.3.3. HYDROFORMYLATION

A hydroformylation reaction involves addition of a hydrogen atom and a formyl group across an olefinic double bond to yield exclusively one or a mixture of two aldehydes, i.e.



(43)

Generally, molecular hydrogen and carbon monoxide are used as the source of these groups, and the primary product of reaction is an aldehyde having one more carbon atom than the olefin substrate. The first hydroformylation catalysts were transition-metal carbonyls such as $Rh_4(CO)_{12}$, $CO_2(CO)_8$. These simple compounds required high operating temperatures (100 - 180^{o}C) and pressures (1500 - 4500 psi) to prevent decomposition. On substitution of carbonyls by phosphine ligands it has been found that catalyst stability varies with the basicity of the organophosphorus group. These modified carbonyl catalysts are influential in product selectivity. Of the two products, normal aldehydes have greater commercial value in view of the demand for n-alcohols prepared from them. Thus, the normal to branched product ratio is important when assessing the usability of a catalyst. The phosphine modified catalysts show a high hydrogenation activity in converting

aldehydes to alcohols, but give markedly slower rates for hydroformylation due to steric hindrance and the increased basicity of phosphine ligands. Thus, good modified hydroformylation catalysts use triphenylphosphine in respect of this ligands low basicity.

Wilkinson and co-workers[115,116] have made extensive studies on the catalyst $RhH(CO)(PPh_3)_3$, and have postulated two mechanisms to explain the essential characteristics of olefin hydroformylation catalysed by rhodium carbonyl phosphine complexes. The first mechanism discussed was an associative process one where there is attack by hydrogen on the monomeric $Rh(CO)_2(PPh_3)_2$ complex, whilst the second mechanism is described as a dissociative process involving loss of a triphenylphosphine ligand from $RhH(CO)_2(PPh_3)_2$.

For each mechanism the oxidative cis-addition of H_2 to a square rhodium(I) complex is assumed to be the rate determining step. Wilkinson et al conclude that both mechanisms can function under the same conditions with the associative mode favoured by excess phosphine presence, whilst the dissociative pathway can operate in the absence of additional phosphine or with high partial pressures of CO. Thus, the associative mechanism will be favoured by addition of phosphine, and experimentally, higher n/i ratios are observed. While phosphine addition reduces the dissociation of $RhH(CO)(PPh_3)_3$, increasing the CO concentration should enhance the dissociative mechanism but will promote formation of a dimer complex $\left[(Ph_3P)_2Rh(CO)_2CO\right]_2$ which plays no part in a hydroformylation reaction.

Of the workers studying anchored hydroformylation catalysts. Pittman et al has made several contributions to the open literature. In a comparison of polystyrene supported analogues of $RhCl(CO)(PPh_3)_2$ and $Co_2(CO)_6(PPh_3)_2$,

the former catalyst gave a superior yield and n/i product ratio (3/1 vs. 2/1) compared to the cobalt system whilst operating at lower temperatures (70 vs. $\approx$150°C) and pressures (400 vs. 1000 psi).[17]

In another paper, Pittman et al[110] used several polystyrene anchored $RhH(CO)(PPh_3)_3$ catalysts for the hydroformylation of 1-pentene. On recycling over ten catalytic runs the activity diminished but selectivity was found to increase with n/i changing from 2.3/1 to 4.4/1 at operating conditions of 60°C and 800 psi of CO/H_2 pressure. This behaviour is due to replacement of PPh_3 ligands by support $-PPh_2$ groups which eventually yields a triply anchored complex $\left[\text{-}(PPh_2)_3\ RhH(CO)\right]$ of lower activity arising from a reduction in unsaturated sites around the rhodium centre.

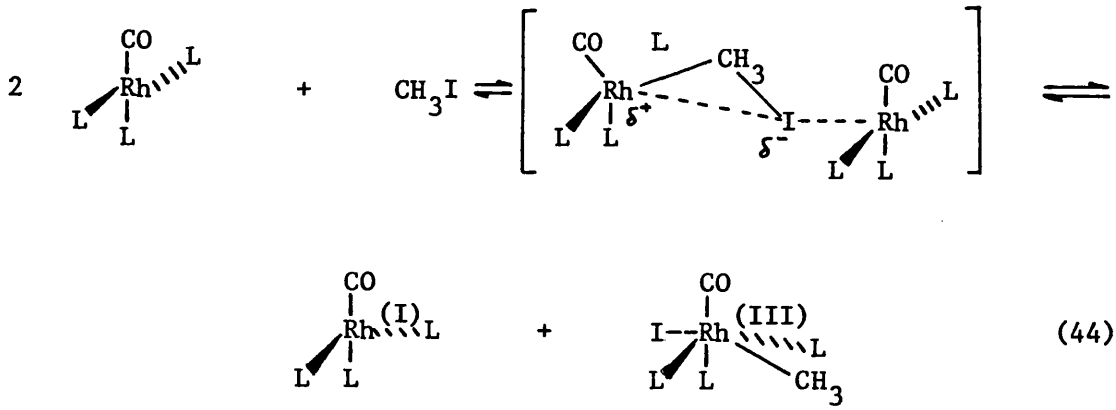
Further studies by Pittman and Hanes[72] on this triply anchored catalyst showed that selectivity was dependent on the temperature and pressure of reaction. A n/i ratio of 16.1/1 compared to 2.2/1 for the homogeneous catalyst $RhH(CO)(PPh_3)_3$ was obtained at 120°C and 100 psi of CO/H_2 pressure. This enhanced selectivity is a result of a greater number of phosphines at or near the rhodium centre from increased polymer mobility at elevated temperatures.

K.G.Allum et al[18,54] of the British Petroleum Company Ltd., also found that hydroformylation studies on 1-hexene using organic polymer and silica supported rhodium catalysts gave comparable results to homogeneous analogues operating at similar reaction conditions. Their reactions were in continuous flow reactors to study the effect of catalyst age on product distribution. The catalyst remained active providing oxygen was excluded from the reactor, otherwise rhodium metal was leached into the fluid products through cleavage of the Rh-P bond by irreversible oxidation. The loss of rhodium was less evident for silica than for

polymer supports, and this stability difference was believed to be attributable to a greater concentration of phosphine ligands relative to rhodium centres on the former support.

1.3.4. CARBONYLATION

Jarrell and Gates[117] have used a supported catalyst for the carbonylation reaction of methanol into acetic acid in the presence of methyl iodide. Their catalyst consisted of a matrix bound rhodium(I) complex formed from a ligand exchange reaction of $Rh(CO)Cl(PPh_3)_2$ with diphenylphosphine groups on a styrene-divinylbenzene copolymer. The authors found the reaction to be second order, while that of the homogeneous complex $Rh(CO)Cl(PPh_3)_2$ was first order, and from their results have proposed an initial step for the mechanism of methanol carbonylation.



(44)

However, the activity of the catalyst progressively diminishes as a result of irreversible conversion of Rh(I) to Rh(III), believed to be by an iodine adduct.

1.4. RESEARCH PROGRAMME USING POLYSILOXANES AS A SUPPORT MATRIX

The previous discussions have indicated the current, widespread interest in the concept of attaching transition-metal complexes to solid/polymer supports for the preparation of active catalysts. This technique combines the selectivity, efficiency and reproducibility of homogeneous catalysts with the thermal stability and separation advantages of heterogeneous systems. The inherent advantages and ease of separation of this class of catalyst can facilitate the use of expensive homogeneous catalysts for general use.

In the reported studies of polymeric and solid supports, many authors have frequently neglected or been unable to give detailed definition of the metal anchoring ligand, and of the active metal centre when in combination with a transition-metal complex. This has led to many idealised formulae being proposed from very limited analytical data.

This research project has involved preparing heterogenised homogeneous catalysts utilising polysiloxanes as the supporting framework. Liquid polysiloxanes offer a number of advantages over conventional solid inorganic and organic polymer supports, such as miscibility with organic solvents, a large liquid range, variable density and viscosity, and both thermal and chemical stability.

A range of model functionalised organosiloxanes have been synthesised each containing a ligand capable of binding a metal containing entity. To these model functionalised siloxanes, a variety of transition-metal complexes have been anchored. The characterisation and structure determination of these model compounds, both metallated and non-metallated, has been by a combination of conventional analytical

techniques which includes nuclear magnetic resonance, infrared spectroscopy and mass spectrometry, and elemental analysis where possible.

The model compounds have acted as synthetic and characterisation aids for a series of ligand functionalised linear polysiloxanes where the distribution of anchor sites within the polymer is known. These polymers are all mobile fluids, soluble in both non-polar and polar organic solvents. From the functionalised linear polysiloxanes, a range of metallated derivatives have been prepared and characterised using the previously mentioned techniques wherever possible.

For a few selected metallated model siloxanes and polysiloxanes, we have undertaken a series of studies to determine their activity as hydrogenation and hydrosilylation catalysts.

CHAPTER TWO

MODEL ORGANOSILOXANES

2.1 INTRODUCTION

Our research programme into the use of polyorganosiloxanes as a support matrix for transition-metal complexes has been divided into four sections. In chronological order these involve the study of model ligands, model complexes, polymers and catalysis which are discussed in Chapters 2 - 5 respectively.

In the initial stages of these investigations a range of functionalised tri-, tetra- and penta-siloxanes containing respectively one, two or three identical substituents have been synthesised. The functionalities contained ligand endings known to interact strongly with transition metals, and included the olefin, arene, cyclohexenyl, pyridine, thiophenol and phosphine entities. These compounds served as models for future syntheses, characterisation and investigations of long chain organofunctional polysiloxanes, and were also used to identify which functionalities were best suited for binding transition metal species of a particular type.

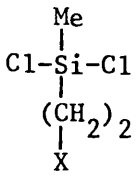
2.2 SYNTHETIC METHODS

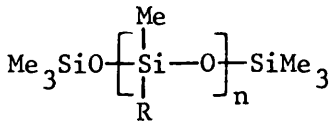
For our studies on model functionalised organosiloxanes, the three commercially available silanes, dichloromethylvinylsilane $SiMeCl_2(CH{=}CH_2)$, dichloromethylallylsilane $SiMeCl_2(CH_2CH{=}CH_2)$, and dichloromethylsilane $SiMeCl_2(H)$ have been used as starting materials. These silanes are readily available at reasonable cost and have proved ideal for further systematic chemical modification either prior to or subsequent on the formation of the Si-O-Si linkage.

We initially wished to synthesise organosiloxanes of general formula $Me_3SiO\left[SiMe(R)O\right]_nSiMe_3$ where n = 1, 2 or 3 and R represents a functional group which may itself act as a potential ligand or contain a ligand ending.

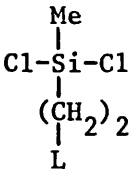
The synthetic procedures used to prepare functionalised organosiloxanes have been extensions of literature methods. Firstly, addition of HX type compounds across the vinyl group of dichloromethylvinylsilane or the allyl moiety of dichloromethylallylsilane which gave rise to functionalised chlorosilanes. These compounds, which have a relatively short alkyl chain separating the silicon centre from the functional group, could be hydrolysed in the presence of chlorotrimethylsilane to form siloxane derivatives. Alternatively, the commercial dichlorosilanes were hydrolysed first to organosiloxanes and then chemically modified to produce a ligating side chain capable of binding transition-metal complexes. A second synthetic approach has involved platinum catalysed hydrosilylation reactions between dichloromethylsilane and 1-alkenes. This synthetic procedure allows a variable alkyl chain spacer link to be formed, and again, these chlorosilanes may be hydrolysed as above to produce organosiloxane derivatives.

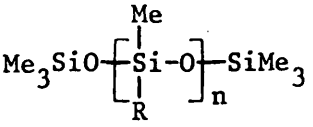
All of the fully characterised dichlorosilanes (1) - (7) and the organosiloxanes prepared from them and the above mentioned silanes are listed below (compounds (8) - (30)) and have the following general formulae.





The reactions of dichloromethylvinylsilane with various HX type compounds has included HC_6H_5, HBr, $HPPh_2$ and C_6H_5SH to produce functionalised dichlorosilanes (1), (5), (6) and (7) respectively in high yield. In each case, anti-Markownikoff addition of HX





	L
(1)	Ph
(2)	CH_2Ph
(3)	CH_2CN
(4)	C_6H_9
(5)	Br
(6)	PPh_2
(7)	SPh

	n	R
(8)	1	$(CH_2)_2Ph$
(9)	2	$(CH_2)_2Ph$
(10)	1	$(CH_2)_3Ph$
(11)	2	$(CH_2)_3Ph$
(12)	1	$(CH_2)_3CN$
(13)	2	$(CH_2)_3CN$
(14)	3	$(CH_2)_3CN$
(15)	1	C_6H_9
(16)	2	C_6H_9
(17)	1	$CH=CH_2$
(18)	2	$CH=CH_2$
(19)	3	$CH=CH_2$
(20)	1	$CH_2CH=CH_2$
(21)	2	$CH_2CH=CH_2$
(22)	1	H
(23)	2	H
(24)	1	$(CH_2)_2Br$
(25)	1	$(CH_2)_3C_5H_4N$
(26)	1	$(CH_2)_2PPh_2$
(27)	2	$(CH_2)_2PPh_2$
(28)	3	$(CH_2)_2PPh_2$
(29)	1	$(CH_2)_3PPh_2$
(30)	1	$(CH_2)_2SPh$

across the vinyl group produced exclusively the terminal adduct. The Friedel Crafts reaction between dichloromethylvinylsilane and benzene was catalysed by aluminium chloride, and the procedure was adapted from the method of Wagner *et al*[118] who previously prepared a trichlorosilane analogue. The bromo derivative (5) was prepared by addition of anhydrous hydrogen bromide in the presence of a peroxide catalyst using a procedure similar to that of Sommer *et al*.[119] The diphenylphosphine (6) and thiophenol (7) derivatives were synthesised using an ultraviolet irradiation technique, and although the former compound has been prepared previously, we later present further characterisation to that stated by the authors concerned.[88]

The alternative procedure involving the platinum catalysed hydrosilylation of 1-alkenes to dichloromethylvinylsilane proved more versatile for the syntheses of a larger range of pure analogues (equation (45)).

$$SiMeCl_2(H) + H_2C{=}CHL \xrightarrow{\text{Pt catalyst}} SiMeCl_2(CH_2CH_2L) \qquad (45)$$

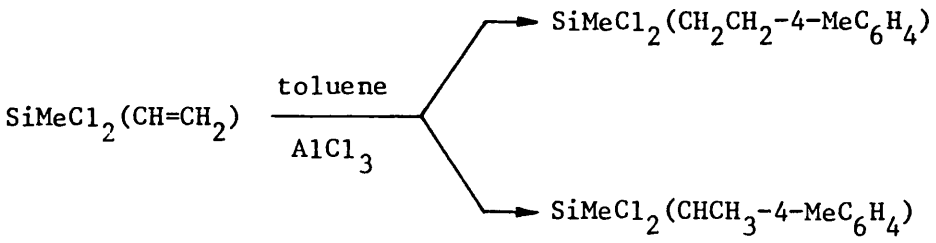
$$(L = CH_2Ph\ (2),\ CH_2CN\ (3),\ C_6H_9\ (4)\ )$$

These reactions are exothermic and rapid, producing chlorosilanes in high yield. The listed silanes are known compounds and include the arene,[120] nitrile[121] and cyclohexyl[121] functionalities. The mechanism by which platinum catalysts promote addition of silicon hydrides to olefins is not fully understood, and it is believed that the silicon group is introduced as an electrophilic moiety R_3Si^+ and the hydrogen atom as a nucleophilic fragment H^-. However, these addition reactions

occur for low concentrations of catalyst and this may support some form of chain mechanism.

All of the dichlorosilane derivatives were isolated as colourless air and moisture sensitive oils by fractional distillation. On standing in air all of the silanes slowly hydrolysed to siloxane condensation products, with the exception of the diphenylphosphine compound which was pyrophoric.

Under Friedel Crafts conditions using aluminium chloride as catalyst, addition reactions between dichloromethylvinylsilane and arenes such as toluene and mesitylene gave mixtures of chlorosilanes from which the desired terminal product could not be isolated in a pure state by fractional distillation (equation (46))

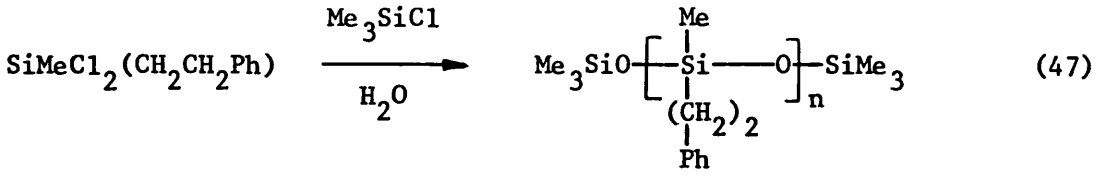


(46)

We find this result difficult to explain in view of the terminal product being formed exclusively with benzene. From our studies we believe that an electronic effect operates from the presence of alkyl groups and consequently influences the course of the reaction. In an attempt to determine whether $AlCl_3$ was influencing the product distribution, we employed two other Lewis acids, $SnCl_4$ and $ZnCl_2$, but no addition products resulted from their use. Musolf and Speier[120] in their reactions of

dichloromethylvinylsilane with substituted styrenes also obtained mixtures of addition products, for example, p-methylstyrene gave only 64% of the terminal adduct.

From the functionalised dichlorosilanes, model organosiloxanes (compounds (8) - (23)) were prepared by hydrolysis in the presence of chlorotrimethylsilane, e.g.



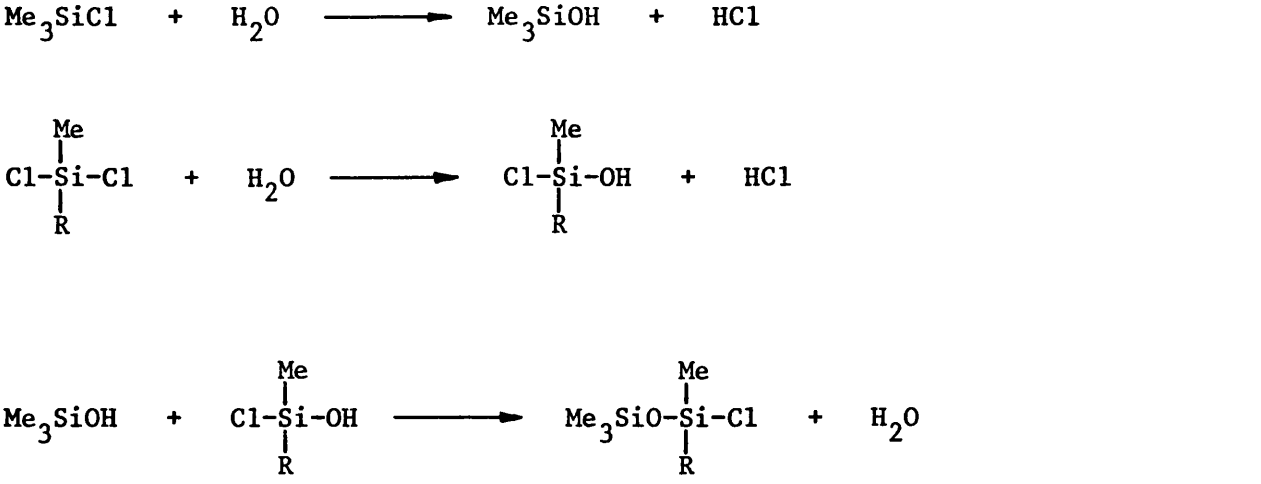
(47)

(n = 1 or 2)

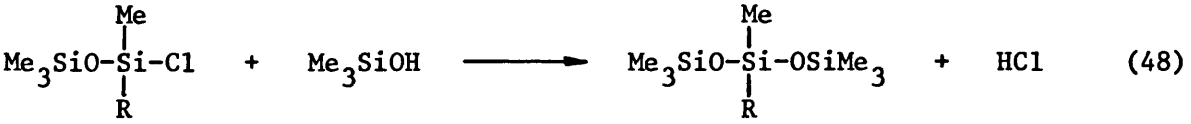
Hexamethyldisiloxane $(Me_3Si)_2O$ was formed as a by-product in each reaction, but the separation of the two series of siloxanes (n = 1 and n = 2) from the reaction mixture was readily achieved by fractional distillation under reduced pressure. Only for the vinyl and nitrile functionalised siloxanes was a third member of the series (n = 3) isolated in a pure state by distillation techniques. A similar hydrolytic procedure has been used previously by Brzezinska and Cullen[88] in the preparation of $Me_3SiO\left[SiMe(CH{=}CH_2)O\right]_nSiMe_3$ (n = 1 or 3) from $SiMeCl_2(CH{=}CH_2)$, but they were unable to isolate the analogue with n = 2, which was the major product formed under our reaction conditions.

The cohydrolysis reaction mechanism to form organosiloxanes having n = 1 and n = 2 etc, consists of a series of nucleophilic additions by silanol species, which are initiated by the presence of water.

A possible mechanism for the formation of an n = 1 siloxane may involve the following steps



(48)



and for an n = 2 species

(49)

Higher siloxanes would result from successive additions of RSi(Me)(Cl)(OH) to the intermediate product of reaction (49).

This method has been used when the functional group present is not susceptible to attack by hydrochloric acid generated during the hydrolysis reaction. The reactions were carried out at low temperature to prevent any significant cleavage of Si-O bonds by the liberated acid. For hydrolysis reactions of this type, organic solvents which can dissolve the siloxane products and yet have a low affinity for water are frequently used for protection purposes. In our hands diethyl ether proved admirable despite the fact that both water and hydrogen chloride are soluble in it. Although siloxane derivatives of (5) and (6) could be prepared by this method,there is a possibility of chemically modifying the ligand functionality. In the case of (6), phosphine oxide formation would yield a highly basic ligand moiety, and for (5) initial substitution by a hydroxyl group could facilitate a cross-linking reaction.

The remaining siloxanes were prepared from other organofunctional siloxanes by substitution of bromide ion in $Me_3SiOSiMe(CH_2CH_2Br)OSiMe_3$ (24), or by addition across the carbon-carbon double bond in vinylsiloxanes (17), (18) and (19).

Compound (24) was prepared by a similar procedure to (5) using an organic peroxide catalysed anti-Markownikoff addition of hydrogen bromide to the vinyl group in (17).

In our early studies on functionalising organosiloxanes, exhaustive attempts were made to prepare siloxyphosphines by bromide ion substitution in (24). For varying reaction times, solvents (thf, diethyl ether, TMEDA) and physical conditions using $NaPPh_2$ and $LiPPh_2$,

we were unable to prepare a phosphine derivative by this procedure. Instead, we generated intractable gums as a result of Si-O bond cleavage and degradation of the trisiloxane backbone to most likely form $\equiv SiOPPh_2$ groups. Interestingly, this reaction has been carried out successfully on both chloromethylated polyphenylsiloxanes [93] and halogen-containing polymethylsiloxanes,[101] without apparently, any such degradation problems.

During studies on this substitution reaction, two preparations were carried out involving bromide ion replacement from an organosilane to serve as a check on the experimental conditions and technique. The organosilane was $Me_3SiCH_2CH_2Br$ (31), which was prepared by low temperature hydrobromination of trimethylvinylsilane using an analogous procedure to that used for the synthesis of compounds (5) and (24). On reaction of (31) with $LiPPh_2$ in thf at 0^oC, the characteristic deep red colouration of the diphenylphosphine ion was discharged rapidly, and following vacuum distillation $Me_3SiCH_2CH_2PPh_2$ (32) was isolated in 63% yield. By a very similar procedure $Me_3SiCH_2CH_2Br$ was reacted with $LiCH_2C_5H_4N$ in thf giving $Me_3SiCH_2CH_2CH_2C_5H_4N$ in 58% yield. Although this latter compound was not characterised by elemental analysis (due to its instability), sufficient evidence for its formation was found from infrared and nuclear magnetic resonance spectral measurements.

By using a similar procedure to that used by Brzezinska and Cullen,[88] tri, tetra and penta-siloxyphosphines were synthesised by the photochemically induced addition of $PHPh_2$ to vinyl siloxanes (17), (18) and (19) (equation (50)), and to an allyl functionalised siloxane (20).

$$Me_3SiO\left[SiMe(CH{=}CH_2)O\right]_nSiMe_3 \xrightarrow[h\nu]{PHPh_2} Me_3SiO\left[SiMe(CH_2CH_2PPh_2)O\right]_nSiMe_3 \quad (50)$$

(n=1, 2, or 3)

As a result of the ease of reaction and high yields found for this synthetic method, all further attempts to prepare these compounds by halogen substitution were abandoned. However, the pyridine derivative (25) was readily prepared by treating $Me_3SiOSiMe(CH_2CH_2Br)OSiMe_3$ with $LiCH_2C_5H_4N$ in thf without any apparent competing degradation reactions (equation (51)).

$$Me_3SiOSiMe(CH_2CH_2Br)OSiMe_3 \xrightarrow{LiCH_2C_5H_4N} Me_3SiOSiMe(CH_2CH_2CH_2C_5H_4N)OSiMe_3 \quad (51)$$

All the siloxane derivatives were air-stable colourless oils with the exception of the bromine, pyridine and phosphine functionalised compounds which are readily oxidised, with the latter type being pyrophoric. The model siloxanes were all soluble in a range of organic solvents including hexane, chloroform, benzene, thf, acetonitrile and acetone, but there was only very limited miscibility with water.

2.3 MISCELLANEOUS AND FAILED REACTIONS

In our syntheses of functionalised trisiloxanes, the metal binding ligand endings which we wished to include but were unsuccessful in preparing were the cyclopentadienyl, isothiocyanate, thiol, acetylacetonate and allyl moieties.

Our efforts to prepare a cyclopentadienyl functionalised trisiloxane derivative were centred on bromide ion substitution from compound (24) using LiC_5H_5, NaC_5H_5 or TlC_5H_5. The reactions were carried out under widely varying conditions and only in one instance using LiC_5H_5 in thf at ambient temperature over four days was a trace of the desired product isolated. In all other cases, after work-up, distillation of the residual mixture yielded only unreacted (24). Attempts to cleave

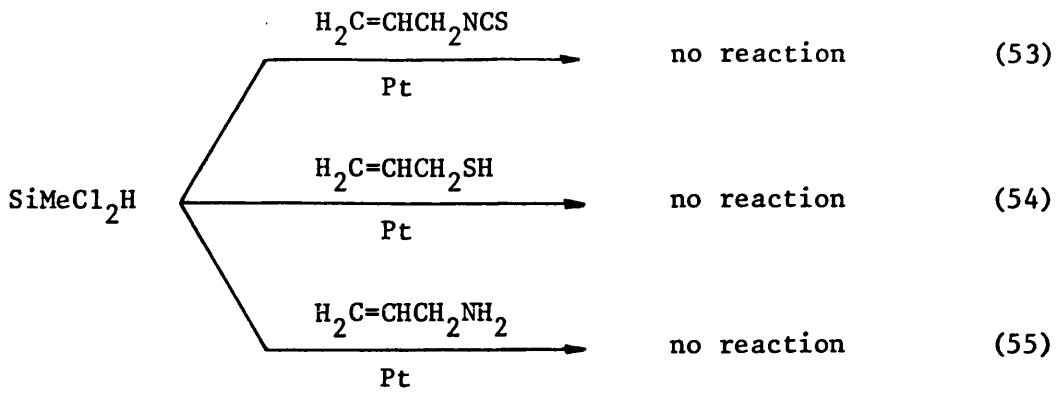
an aromatic C-Br linkage were also unsuccessful. The compound $Me_3SiOSiMe(CH_2CH_2\text{-}4\text{-}BrC_6H_4)OSiMe_3$ was prepared by the platinum catalysed hydrosilylation of dichloromethylsilane with 4-bromostyrene according to the method of Musolf and Speier,[120] followed by cohydrolysis with chlorotrimethylsilane in diethyl ether/water. The terminal adduct was present to ca 75% as a mixture with the Markownikoff substitution product $Me_3SiOSiMe(CHCH_3\text{-}4\text{-}BrC_6H_4)OSiMe_3$, and was used directly in similar reactions to those described above. No substitution product was isolated in each case.

Another route employed to prepare a cyclopentadienyl functionalised trisiloxane was a two step synthesis involving chloromethylation of the phenyl ring at the 4-position followed by reaction with lithium cyclopentadienide (equation (52))

$$(Me_3SiO)_2SiMe(CH_2CH_2C_6H_5) \xrightarrow[\text{catalyst}]{ClCH_2OCH_3} (Me_3SiO)_2SiMe(CH_2CH_2\text{-}4\text{-}C_6H_4CH_2Cl) \quad (52)$$

Attempts to prepare the chloromethylated product using chloromethyl-methylether in the presence of $SnCl_4$ or $ZnCl_2$ as catalyst by an adaption of the method of Kennedy et al[122] were unsuccessful, and no reaction was observed in all cases.

In view of the ease with which dichloromethylsilane reacted with 4-vinylcyclohexene to produce compound (4) in high yield, we attempted to use this silane in a series of further platinum catalysed hydrosilylation reactions with the following allyl compounds (equations (53)-(55)). The reaction conditions of vigourous heating under reflux over several days using chloroplatinic acid or platinum on carbon failed to produce any functionalised dichlorosilane products. In the case of allylamine, we believe an aminehydrochloride derivative was produced through reaction

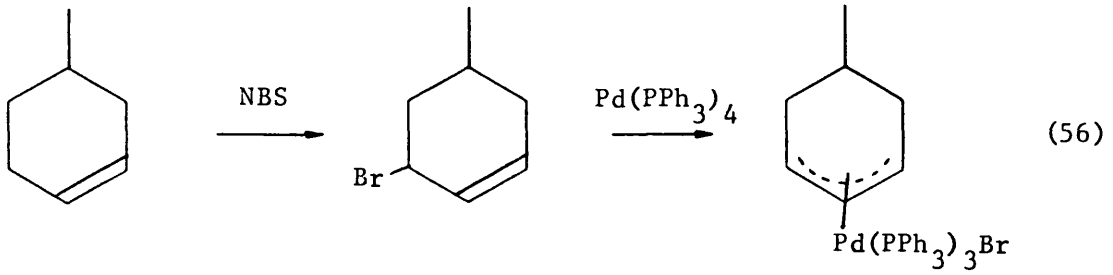


of the amine group with reactive Si-Cl bonds. On substituting dichloromethylsilane for $Me_3SiOSiMeHOSiMe_3$, no aminehydrochloride or addition product resulted. A further attempt to prepare an isothiocyanate functionalised siloxane was by the photochemical reaction between allyl-isothiocyanate and $Me_3SiOSiMeHOSiMe_3$ (22). No reaction was evident after irradiation for 48h. This experimental procedure was not employed for reaction of allylamine or allylmercaptan with (22), in view of their low boiling points.

Our attempts to prepare an acetylacetonate functionalised siloxane of general formula $Me_3SiOSiMe\left[(CH_2)_xCH(COCH_3)_2\right]OSiMe_3$ (x=2 or 3) using two synthetic routes were also unsuccessful. By similar procedures to those described previosly for bromide substitution reactions, $Me_3SiOSiMe(CH_2CH_2Br)OSiMe_3$ repeatedly failed to react with sodium acetylacetonate. The alternative method of SiH addition to $H_2C=CHCH_2CH(COCH_3)_2$ seemed attractive, but several attempts to synthesise $H_2C=CHCH_2CH(COCH_3)_2$ using the method of English et al,[123] failed to produce an analytically pure sample of this compound. On reaction of the crude material with (22) in the presence of platinum on carbon, the addition product, which was identified only by ^1H n.m.r. spectroscopy, was isolated as a lemon yellow oil in very low yield (ca 7%) by vacuum distillation. However, as a result of the low yield and rapid

decomposition of the product at $0^{o}C$ under N_2, all further studies on this species were abandoned.

Our efforts to prepare a functionalised siloxane which could anchor transition-metal complexes through an allyl moiety were conducted through the cyclohexenyl group of compound (15), i.e.



(56)

Following allylic bromination of (15) with N-bromosuccinimide (NBS) in carbon tetrachloride using a benzoyl peroxide catalyst, a mixture of unstable bromination products formed which were not separable by distillation. No further attempts were made to modify the route.

As a result of producing a mixture of chlorosilanes from the Friedel Crafts reaction of dichloromethylvinylsilane with mesitylene, and subsequently an analogous mixture of siloxanes from hydrolysis with chlorotrimethylsilane, we attempted to prepare the siloxane derivative by a one-step reaction between $Me_3SiOSiMe(CH=CH_2)OSiMe_3$ (17) and the arene using similar experimental conditions. By using a compound where the vinyl group appears more sterically hindered we hoped to increase or form exclusively the anti-Markownikoff addition product. However, no addition reaction was evident from spectroscopic analysis, and this result also applied when benzene was used.

2.4 SPECTRAL CHARACTERISATION OF ORGANOSILANES AND ORGANOSILOXANES

The use of spectroscopic techniques (Appendix I) has proved invaluable for the identification and characterisation of all the organofunctional dichlorosilanes and siloxanes prepared in the course of these studies. In both infrared and nuclear magnetic resonance spectra respectively, the absorptions and resonances that are characteristic of the functional group present are generally well separated from those signals of the siloxane backbone, and this has made characterisation a relatively simple task.

2.4.1 INFRARED SPECTROSCOPY

The infrared spectra for both dichlorosilanes and siloxanes have been measured as neat samples between NaCl discs, and the results have been used for qualitative analysis of the components present in each compound. A general summary of the relevant infrared absorptions found for compounds of this type are listed in Table 2.1 with assignments based on earlier studies by Lee-Smith.[124] Tables 2.2 and 2.3 summarise the characteristic absorption frequencies for a selection of chlorosilanes and model organosiloxanes respectively. Figures 2.1 to 2.3 illustrate representative spectra.

Table 2.1 Summary of infrared absorptions for organosilanes and organosiloxanes

Group	Infrared absorption (cm^{-1})	Assignment
MeSi	3000-2850	C-H stretch
	1440-1390	C-H antisymmetric bending mode
	1280-1240	C-H symmetric bending mode
	870-750	Me rocking vibration
	865-715	Si-C stretch
Me_2Si	850, 800	Me rocking vibration
Me_3Si	840, 760	Me rocking vibration
Me_3SiO	845, 745	Si-C stretch
Si-H	2300-2100	Si-H stretch
Si-O-Si	1130-1000	Si-O-Si antisymmetric stretch
$Si-CH=CH_2$	1600	C=C stretch
SiCl	620-420	Si-Cl stretch

Table 2.2 Summary of infrared absorption frequencies for selected chlorosilanes

Compound	Infrared absorption frequency (cm^{-1})
(1)	3105sh, 3082sh, 3063m, 3026s, 2923s, 2862m, 1601m, 1581w, 1498s, 1455s, 1403s, 1320w, 1261vs, 1182s, 1160sh, 1122m, 1062w, 1030m, 996m, 921sh, 900s, 835vs, 803vs, 789vs, 770vs, 760sh, 743vs, 702vs, 652s
(4)	3027m, 2922vs, 2887sh, 2852sh, 1652w, 1447m, 1438m, 1403m, 1335w, 1261vs, 1205m, 1173m, 1142m, 1040m, 948w, 922m, 870m, 820s, 790vs, 753m, 657s
(5)	2961w, 2903w, 1440w, 1412m, 1400sh, 1382sh, 1201vs, 1161m, 1150w, 1082m, 1022s, 1008sh, 871m, 818vs, 802vs, 792vs, 773s, 754s, 694m, 651m
(7)	3075m, 3065m, 3025w, 2965w, 2930m, 2890sh, 1585s, 1482s, 1440s, 1406m, 1279s, 1261vs, 1164s, 1088s, 1066s, 1024s, 1004s, 874m, 818sh, 805vs, 784vs, 737vs, 687vs

Table 2.3 Summary of infrared absorption frequencies for selected organosiloxanes

Compound	Infrared absorption frequency (cm^{-1})
(8)	3070w, 3035m, 2965vs, 2898m, 1605w, 1495m, 1456m, 1412m, 1262vs, 1180m, 1050vs, 842vs, 796s, 784s, 757s, 700s
(12)	2964s, 2903m, 2250w, 1455w, 1431m, 1420m, 1345w, 1260vs, 1178m, 1050vs, 845vs, 786s, 756s, 690m, 657m
(15)	3032m, 2965s, 2927s, 2888sh, 2850m, 1652w, 1456m, 1440m, 1412m, 1336w, 1260vs, 1204m, 1175m, 1142sh, 1050vs, 921w, 844vs, 817s, 781s, 757s, 693m, 656m
(17)	3050m, 3018w, 2960vs, 2902m, 1597m, 1409s, 1255vs, 1050vs, 1015s, 960m, 874vs, 842vs, 795vs, 757vs, 688m, 630m
(20)	3082w, 2968s, 2903w, 1635m, 1438w, 1418w, 1260vs, 1160m, 1055vs, 993m, 935m, 896m, 873s, 841vs, 808s, 786s, 756s, 687m, 640w
(22)	2960s, 2898w, 2160vs, 1405w, 1256vs, 1050vs, 917s, 890s, 840vs, 765s, 688w
(24)	2963s, 2910m, 1445w, 1404m, 1260vs, 1158m, 1060vs, 1032sh, 848vs, 796s, 758s, 691m, 639m
(25)	3069w, 3020w, 2963s, 2934sh, 2915sh, 2866sh, 1602m, 1559w, 1487w, 1442m, 1414m, 1376w, 1255vs, 1214w, 1176sh, 1060vs, 866m, 841vs, 786s, 756s, 690m, 646w

Table 2.3 (cont.)

(26)	3071w, 3050m, 2960vs, 2898m, 1582w, 1475m, 1430s, 1408m, 1255s, 1195w, 1145s, 1050vs, 995m, 838vs, 790s, 778s, 750s, 735s, 715m, 692vs, 625w, 502m, 475w, 362w, 296w
(30)	3075w, 3065w, 2962s, 2930m, 2896m, 1585m, 1482m, 1440m, 1406w, 1261vs, 1164m, 1060vs, 1022sh, 1008s, 841vs, 795s, 752s, 736s, 696s

The structurally simplest trisiloxane prepared in our series has been $Me_3SiOSiMe(H)OSiMe_3$ (22), and its infrared spectrum (Figure 2.1) serves as a useful model for identifying characteristic siloxane absorptions. The strong band at 2960 cm^{-1} (range 2850-3000 cm^{-1}) are assigned to the C-H stretching mode of the methyl groups. The broad, yet relatively weak band at 1405 cm^{-1} (within an absorption range of 1390 −1440 cm^{-1}) represents an asymmetric Me deformation of SiMe, whilst the intense, sharp band at 1260 cm^{-1} (range 1240-1280 cm^{-1}) is the corresponding symmetric deformation. The Si-O-Si absorption appears as a very broad and intense band centred at 1050 cm^{-1}. This band can vary between 1130-1000 cm^{-1} and is dependent on the mass and inductive effects of other groups bonded to silicon. Furthermore, as the siloxane chain increases in length this absorption may split into two overlapping bands. The strong bands at 840 and 765 cm^{-1} (range 870-750 cm^{-1}) are attributed to methyl group rocking vibrations, and always accompany the C-H symmetric bending mode. The single methyl group on silicon gives a band at about 775 cm^{-1}. Finally, the intense bands at 2160 and 917/890 cm^{-1} are Si-H stretching and bending modes respectively.

As well as the assignments made previously, the functional group in each compound also exhibits characteristic absorptions, for example, in compound (26) (Figure 2.2) the diphenylphosphine ligand shows aromatic C-H stretching and C=C skeletal stretching at 3071/3050 and 1582/1475 cm^{-1} respectively. Three weak aromatic summation bands are also observed between 1800 and 1950 cm^{-1}, whilst absorptions indicative of monosubstitution on a phenyl ring are seen at 750 and 692 cm^{-1}. For $Me_3SiOSiMe(CH_2CH_2CH_2C_5H_4N)OSiMe_3$ (25), absorptions due to the pyridine ligand are observed at 3069/3020, 1602 and strongly at 1559 cm^{-1} representing aromatic C-H, C=N and C=C stretching respectively. C-H

deformation of the hetero-aromatic ring occur at 786 and 756 cm^{-1}. On comparism of this siloxane to its silane analogue $Me_3SiCH_2CH_2CH_2C_5H_4N$, only small changes in the respective absorptions are observed, 3070/3025, 1605 and 1559 cm^{-1}. Other notable infrared absorptions are : C≡N at 2250 cm^{-1} in $Me_3SiOSiMe(CH_2CH_2CH_2CN)$ (Figure 2.3); C=C at 1597 cm^{-1} in $Me_3SiOSiMe(CH=CH_2)OSiMe_3$; C=C at 1635 cm^{-1} in $Me_3SiOSiMe(CH_2CH=CH_2)OSiMe_3$; C-H at 3070 and 3035 cm^{-1}, and C=C at 1605 and 1495 cm^{-1} in $Me_3SiOSiMe(CH_2CH_2C_6H_5)OSiMe_3$; C=C at 1585 and 1482 cm^{-1} in $Me_3SiOSiMe(CH_2CH_2SC_6H_5)OSiMe_3$. On comparing the infrared spectra of organosiloxanes of general formula $Me_3SiO\left[SiMe(R)O\right]_nSiMe_3$ (n = 1, 2 or 3) which were measured under identical conditions, there were no significant changes in absorption frequencies, but only changes in relative intensities between individual members. Similarly, no obvious changes were observed for siloxanes possessing identical functional groups but being separated from the silicon centre by different alkyl chain lengths, e.g. compounds (8) and (10), (9) and (11), (26) and (29).

2.4.2 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

The good miscibility of chlorosilanes and organosiloxanes with deuterated solvents has enabled us to record ^1H, ^{13}C, and for one series of compounds ^{29}Si n.m.r. spectra (courtesy of the high field n.m.r. service at Warwick University). The n.m.r. spectral data for chlorosilanes and organosiloxanes are listed in Tables 2.4 and 2.5 respectively. For compounds which were air and moisture sensitive, spectra were recorded under N_2 in degassed deuterochloroform. Figures 2.4 - 2.7 represent ^{13}C n.m.r. spectra for compounds (10), (20), (25) and (26) respectively.

Silicon compounds frequently display a pair of ^{29}Si satellites about the centre resonances in n.m.r. spectra and are a consequence of the

Table 2.4 1H and 13C n.m.r. data for selected silanes

SILANE	SiMe	C1/H1	C2/H2	C3/H3	OTHERS	AROMATICS
(1)	0.64(3H, s) 5.17	1.42(2H, m) 23.42	2.81(2H, m) 28.46			7.20(5H, m) 126.1, 127.8, 128.5, 142.3
(2)	0.32(3H, s) 4.98	0.72(2H, m) 20.96	1.40(2H, m) 24.16	2.25(2H, m) 38.19		6.70(5H, s) 125.4, 125.95, 128.34, 141.12
(3)	0.80(3H, s) 5.04	1.26(2H, m) 19.12	1.86(2H, m) 19.50	2.24(2H, t) 20.59	118.86(CN)	
(4)	0.76(3H, s) 5.00	1.06(2H, m) 17.87	 28.85		1.50(9H, m) 5.65(2H, m) 25.10, 27.30, 31.38, 35.61, 126.14, 126.50, 126.90	
(5)	0.87(3H, s) 5.69	1.90(2H, m) 25.95	3.60(2H, m) 27.14			
(6)	0.72(3H, s) 4.87	1.21(2H, m) 11.06(12.21)	2.20(2H, m) 19.83(12.21)			7.16(10H, m) 128.64(d, 13.43), 132.59(d, 18.31), 136.63(d, 9.76), 130.69(d, 8.54)
(7)	0.92(3H, s) 5.49	1.60(2H, m) 21.80	3.21(2H, m) 27.43			7.20(5H, m) 126.30, 128.95, 129.55, 135.40
(31)	0.02(9H, s) -1.79	1.38(2H, m) 24.00	3.58(2H, m) 31.47			
(32)	0.02(9H, s) 1.90	0.60(2H, m) 14.14(9.76)	1.02(2H, m) 23.67(14.65)			7.10(10H, m) 130.18(d, 7.33), 130.23, 134.60(d, 18.31), 140.96(d, 14.65)

Table 2.5 1H and 13C n.m.r. data for selected organosiloxanes

	OSiMe	SiMe	C1/H1	C2/H2	C3/H3	OTHERS	AROMATICS
(8)	0.10(18H, s) 1.90	0.10(3H, s) -0.27	0.80(2H, m) 19.80	2.64(2H, m) 29.40			7.18(5H, m) 145.1, 128.3, 127.9, 125.5
(10)	0.07(18H, s) -0.19	0.07(3H, s) -0.10	0.45(2H, m) 17.50	1.60(2H, m) 25.20	2.58(2H, m) 39.50		7.12(5H, s) 142.7, 128.5, 128.3, 125.7
(12)	0.54(18H, s) 1.54	0.48(3H, s) -0.57	1.04(2H, m) 16.80	2.13(2H, m) 19.80	2.80(2H, t) 20.20	119.3(CN)	
(15)	0.08(18H, s) 1.57	0.08(3H, s) -0.32	0.48(2H, m) 14.70	1.30(2H, m) 30.30		1.80(7H, m) 5.64(2H, m) 25.5, 28.7, 31.8, 36.4, 126.70, 127.00	
(17)	0.46(18H, s) 2.31	0.46(3H, s) 0.00	6.25(3H, m) 137.50	 132.00			
(20)	0.12(18H, s) 2.71	0.12(3H, s) 0.01	1.51(2H, d) 26.70	5.80(1H, m) 135.00	4.88(2H, m) 114.50		7.16(10H, m) 136.63(d, 9.76), 132.59(d, 18.31), 130.69(d, 8.54), 128.64(d, 13.43)
(22)	0.56(18H, s) 1.64	0.53(3H, s) 1.32				5.10(1H, m)	7.20(5H, m) 135.40, 129.55, 128.95, 126.30
(24)	0.54(18H, s) 1.84	0.54(3H, s) 0.49	1.74(2H, m) 25.10	3.94(2H, m) 30.10			
(25)	0.05(18H, s) 0.16	0.05(3H, s) 0.00	0.46(2H, m) 17.40	1.65(2H, m) 24.30			7.02(2H, d) 8.41(2H, d) 151.4 , 149.9, 124.1
(26)	0.08(18H, s) 1.90	0.08(3H, s) -0.49	0.56(2H, m) 13.20(d, 9.8)	2.02(2H, m) 21.00(d, 14.7)			7.28(10H, m) 139.2(d, 13.7), 134.0(d, 17.1) 132.8(d, 18.3), 128.3(d, 3.7)
(29)	0.06(18H, s) 2.06	0.06(3H, s) 0.22	0.67(2H, m) 19.70(d, 10.3)	1.54(2H, m) 19.90(d, 12.7)	2.12(2H, m) 32.70(d, 13.1)		7.38(10H, m) 139.4(d, 13.1), 134.1(d, 17.1) 132.9(d, 17.1), 128.5(d, 3.7)
(30)	0.31(18H, s) 1.65	0.31(3H, s) -0.11	1.10(2H, m) 17.03	3.16(2H, m) 28.36			7.41(5H, m) 136.92, 129.01, 128.63, 125.59

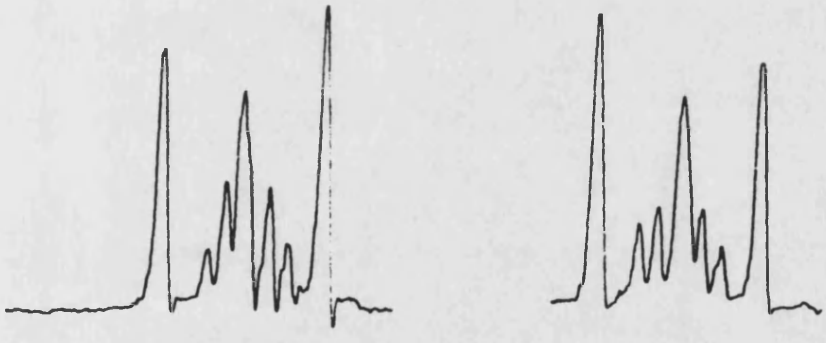
spin isotope ($I=\frac{1}{2}$) and 4.7% natural abundance. These satellites must be considered in quantitative analysis of spectra.

The ^{1}H n.m.r. spectra for chlorosilanes (1), (2), (3), (4) and (6) have been reported,[88,120,121] but to our knowledge their ^{13}C n.m.r. spectral parameters have not appeared in the literature. The ^{1}H and ^{13}C n.m.r. spectra for both classes of compound show similar characteristics, with resonances for the siloxane backbone ($SiMe/Me_3Si$), the alkyl spacer chain ($(CH_2)_x$) and the functional group generally being well separated. This, together with the use of an INEPT[125] (insensitive nuclei enhancement polarisation transfer) sequence onour ^{13}C n.m.r. spectrometer provided a simple method of distinguishing between CH/CH_3 and CH_2 moieties in both aliphatic and aromatic environments, which enabled straightforward identification of spectral resonances. The ^{13}C and ^{29}Si n.m.r. of linear, branched and cyclic methyl and poly(methylsiloxanes) have been reported by several workers,[126-129] however, the spectral data of discrete organosiloxane molecules[130] and polymer analogues are seldom found in the open literature and consequently very few comparisms can be made.

For chlorosilanes (1), (4), (5), (6), (7), and organosiloxanes (8), (15), (24) and (30) where there is a two carbon atom spacer chain between silicon and the functional group, the proton n.m.r. spectra for the methylene groups are characteristic of an A_2X_2 splitting pattern. This is a consequence of the chemical shift difference between the two groups being large compared to the coupling constant. Since the addition reactions for their formation all gave the terminal product, these resonances were not complicated by the presence of signals from CH and CH_3 moieties which would result from internal addition. A typical A_2X_2 system should consist of two bands each containing a maximum of ten lines.[131] The spectrum is also characterised

by symmetry about the mid-point of the resonance so that the band of the A group is the mirror image of that of the X group. As a result of the symmetry of an A_2X_2 system only one of the bands, A or X, need be discussed. There are four coupling constants, $J_{AA'}$, $J_{XX'}$, $J_{AX'}$ and $J_{A'X}$ which determine the separation and intensities of the components of each band. McConnell *et al*[132] have derived expressions for separations and intensities. The simplest case is where $J_{AX} = J_{A'X}$. For this case the spectrum can be correctly predicted from simple splitting rules.

Figure 2.8 Partial ^1H n.m.r. spectrum of $Me_3SiOSiMe(CH_2CH_2SPh)OSiMe_3$ illustrating methylene group resonances



For the previously mentioned chlorosilanes and organosiloxanes, and for the silane $Me_3SiCH_2CH_2Br$ (31), symmetrical bands each consisting of seven lines are observed. This is illustrated for $Me_3SiOSiMe(CH_2CH_2SPh)OSiMe_3$ in Figure 2.8.

The large separation in chemical shifts for the methylene protons arises from deshielding and shielding effects. Groups such as C_6H_5, SC_6H_5,

Br and PPh_2 have a deshielding influence on adjacent methylene protons and cause them to resonate at lower field. Conversely, the silicon centre shields neighbouring methylene protons, thus promoting a shift to higher field.

On comparing the ^1H and ^{13}C spectra for identical groups in both chlorosilanes and organosiloxanes derived from them, the major shift changes occur for SiMe and C_1/H_1 as a result of a new shielding influence operating when Si-Cl bonds are substituted by $Si-OSiMe_3$. For example, the shift changes for $SiMeCl_2(CH_2CH_2Ph)$ and $Me_3SiOSiMe(CH_2CH_2Ph)OSiMe_3$ can be seen in Table 2.6. The ^1H n.m.r. spectra of the (trimethylsilyl) and (dichloromethylsilyl) derivatives show single resonances for the SiMe group.

Table 2.6. ^1H and ^{13}C n.m.r. data for compounds (1) and (8).

	Chemical shift (ppm)			
	^1H		^{13}C	
Compound	SiMe	H_1	SiMe	C_1
(1)	0.64	1.42	5.17	23.42
(8)	0.10	-0.27	0.80	19.80

The effect of increasing the spacer arm length in $Me_3SiOSiMe\left[(CH_2)_xL\right]OSiMe_3$ (x=2 or 3) only causes changes in the chemical shifts of comparable methylene groups. For example, comparing compound (8) with (10) the overall ^{13}C and ^1H n.m.r. resonances shift by δ 2.38 and 0.35 for C_1/H_1, and for the methylene group adjoining the phenyl ring the shift change is 10.1 and 0.06 respectively. In the proton n.m.r. spectrum

the H_1 protons are observed as apparent triplets with fine structure, and for our analysis are designated multiplets. Only in compounds (25), (12) and (10) are true triplets seen for the H_3 resonance, whereas the H_2 resonance is a broad unresolved multiplet in all cases.

The resonances for the pyridine ring protons are an example of an AA'XX' splitting pattern, with the resonance at 8.41 representing two protons in the α-position to the nitrogen atom, whilst the β-protons are at δ 7.02. The ^{13}C-^{1}H coupling for both doublets is 4.7 Hz.

The vinylsiloxane (17) has been prepared previously,[65] and its ^{1}H and ^{13}C n.m.r. spectral data have been reported.[133] In the proton n.m.r. spectrum the vinyl group splitting pattern is complex, typical of an ABC spin system where a maximum of 14 observable bands are expected,[134] but usually only 10 are seen.[135] However, the vinyl signal often reduces to a singlet[135] because of accidental equivalency from other electronegative groups on silicon, and this was found for compound (17). The phosphine (26) derived from (17) has also been prepared, and we report detailed ^{13}C n.m.r. spectral data in Table 2.7. This compound, and its higher analogues (18) and (19), all show characteristic coupling between the ^{31}P nucleus with the methylene and aromatic carbon atoms.

Table 2.7 ^{13}C n.m.r. data for compound (26)

Carbon atom	^{13}C n.m.r. chemical shift	$J(^{13}C-^{1}H)$ (Hz)
3	139.2	(13.7)
4/4'	132.8	(18.3)
5/5'	128.3	(3.7)
6	134.0	(17.1)

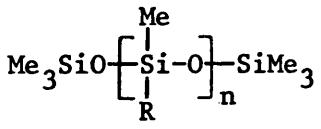
The methylene resonances appear as well resolved doublets with coupling constants up to 14.7 and 9.8 Hz for the $-CH_2P$ and $SiCH_2$ moieties respectively. Although the aromatic signals for (26) can be readily identified, complete interpretation for compounds (27) and (28) has proved difficult owing to complicated splitting patterns arising from higher order phosphorus coupling. For the proton n.m.r. spectra, both the aromatic and methylene group resonances are poorly resolved, and there were no significant improvements on ^{31}P decoupling.

From studies made on various cyclotetrasiloxanes and cyclopolymethylphenylsiloxanes,[136] analysis of the SiMe resonance in the ^1H n.m.r. spectra can reveal isomers from shift-structure correlations. Pelletier and Harrod[137] have used a simple empirical approach based on the chemical environment of the resonating protons to assign ^1H n.m.r. spectra of isomers of substituted methylcyclosiloxanes of general formula $(SiMeRO)_n$, where R = Me, Ph, Br and H. For R = H and n = 5, the authors observed the SiH moiety as a complicated multiplet, whilst the SiMe region showed the superposition of a complex cluster of peaks. This complexity is partially due to coupling between the protons of the geminal methyl group and the hydrogen bonded to silicon. We have observed similar coupling effects in the proton spectra of siloxanes (22) and (23), $Me_3SiO(SiMeHO)_nSiMe_3$, where n = 1 and 2 respectively. In both cases the SiH proton resonance is an unresolved multiplet in the region 5.0-5.1 ppm, whereas for the SiMe resonance, although partially masked by the $OSiMe_3$ resonance, other signals are observed but only for the higher siloxane. Thus, although complex signals are only clearly seen for the SiH proton, this is sufficient evidence for three-bond coupling through the Me-Si-H moiety, where hydrogen has a net through-space deshielding effect compared to the methyl group itself. The ^{13}C n.m.r. spectra showed single resonances for the SiMe

and $OSiMe_3$ groups, and consequently no $^{13}C-^{1}H$ coupling was observed.

The proton n.m.r. spectrum of $Me_3SiOSiMe(CH_2CH=CH_2)OSiMe_3$ (20) shows three well separated resonances for the components of the allyl group. The $SiCH_2$ signal is a well resolved doublet at δ 1.51, but the $(-CH=CH_2)$ group shows two complex unresolved multiplets at δ 4.88(2H) and δ 5.80 (1H). Although individual resonances have been assigned, full interpretation has not been possible as a result of high order coupling effects.

The n.m.r. spectroscopic data on the three series of compounds (A), (B) and (C) are very similar,



n = 1, (A); n = 2, (B); n = 3, (C)

and only in compounds (9) and (14) were we able to detect any signs of separate n.m.r. signals for the two or four diastereoisomers expected for compounds of type (B) or (C) respectively, and then only in the MeSi region of their ^{13}C n.m.r. spectra where additional shoulders were observed compared with the spectra of compounds of type (A).

For the nitrile series of compounds $Me_3SiO\left[SiMe(CH_2CH_2CH_2CN)O\right]_nSiMe_3$ (n = 1, 2 or 3), ^{29}Si n.m.r. spectra have been recorded and chemical shift data is reported in Table 2.8. For ^{29}Si n.m.r. the magnetic moment and spin of the ^{29}Si nucleus are antiparallel, and this results in a negative sign for the gyromagnetic ratio γ. If relaxation of the ^{29}Si nucleus depends exclusively on dipole-dipole interactions, then in some cases strong negative ^{29}Si signals can result. We have observed

this for MeSiO groups in all samples as asingle resonance. A zero signal is also possible and has been well documented.[138] ^{29}Si n.m.r. has shown the discrimination between end (R_3SiO), chain (R_2SiO_2), branch ($RSiO_3$) and quaternary (SiO_4) units in siloxanes. This is based on the fact that ^{29}Si resonance frequencies are very dependent on the number of oxygen atoms bonded to the silicon centre. The range of ^{29}Si chemical shifts covers about 400 ppm, and ranges for the above moieties are listed in Table 2.9.

Table 2.8 ^{29}Si n.m.r. data for $Me_3SiO\left[SiMe(CH_2CH_2CH_2CN)O\right]_nSiMe_3$

Compound	(ppm) M	D	D'
(12) MDM	17.868	-13.567	-
(13) MD_2M	18.327	-13.713	-
(14) MDD'DM	18.330	-13.446	-13.739

(M = Me_3SiO, D = silicon centre for nitrile group)

Table 2.9 ^{29}Si n.m.r. chemical shifts for R_xSiO_y

Silicon group	(ppm) Range	Mean value
R_3SiO	-44 to +44	12
R_2SiO_2	-74 to +14	-20
$RSiO_3$	-99 to -37	-57

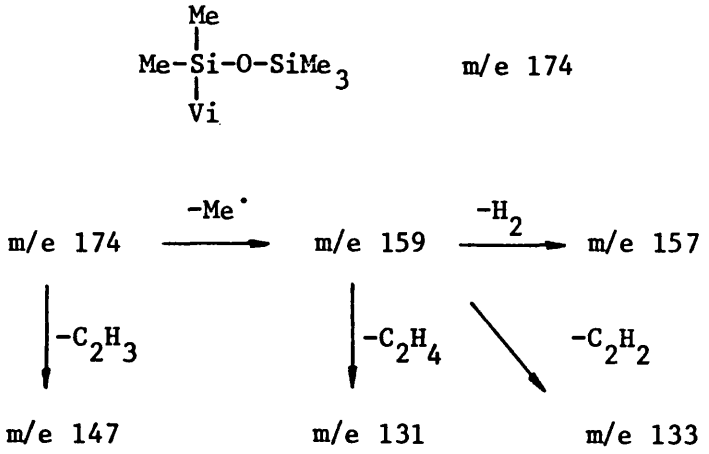
For the nitrile functionalised tri-, tetra- and pentasiloxanes, each silicon centre is flanked by two oxygen atoms with the groups attached through these atoms being either an end-blocking trimethylsilyl (Me_3Si) or a silicon centre for a nitrile group $SiMe(CH_2CH_2CH_2CN)O$. However, only small changes in chemical shift were found for the D and M units present in these compounds as a result of similar environments surrounding each centre.

2.4.3 MASS SPECTROMETRY

With afew exceptions the literature on the mass spectra of siloxanes is limited to studies on small linear, cyclic, and long-chain linear siloxanes.[139-141] Consequently, the mass spectra of the more volatile siloxanes prepared in our studies Type (A) : (8), (10), (12), (15), (17), (20), (24), (26), (30) ; Type B : (9), (13), (18), (27) ; Type (C) : (14), (19) have been recorded, and spectral data is reported in Tables 2.10 and 2.11. Figures 2.9 - 2.13 represent mass spectra of compounds (8), (9), (12), (14) and (26) respectively.

A feature common to the fragmentation patterns of methylsiloxanes is the facile loss of $Me^{\cdot}$ from the quaternary silyl centre of the parent ion to form an $(M - 15)^+$ fragment. Doubly charged and metastable ions are also invaluable aids in structure determination. The mass spectra of methylcyclosiloxanes have been well documented,[142] and linear dimethylsiloxanes show many analogies to this class of compound. Similarly, the spectra of siloxanes which contain substituents other than methyl attached to silicon show decomposition processes which are characteristic to those of both linear and cyclic siloxanes. However, when methyl groups are replaced by larger organic substituents, losses through rearrangements of these groups tend to be more frequent. For

example, consider the decomposition pathways of vinylpentamethyl-disiloxane. As well as direct cleavage of methyl and vinyl moieties, there are rearrangement losses of ethylene, acetylene and hydrogen, i.e.



(Vi = vinyl)

For many of the siloxanes studied, we have found a high selectivity in the dissociation pathways followed. The intensities of the molecular ions were invariably low, and in several cases were absent. However, in chemical ion (C.I.) spectra (with the exception of compound (24)) $(M + H)^+$ ions were clearly seen. The $(M - Me)^+$ peaks are among the most intense observed, and fragmentation from this ion was a common feature in our studies. This has also been reported by Orlov[142] and Swaim et al[143] for their E.I. studies on methylsiloxanes and arylsiloxanes respectively. Other evident features are the high intensity peaks for $(Me_3Si)^+$ m/e 73, $(Me_2SiH)^+$ m/e 59, and in some cases $(MeSiH_2)^+$ m/e 45, which have also been observed by Pelletier and Harrod.[140] For functionalised organosiloxanes a number of the fragment

ions are formed by elimination of hydrocarbon groups from the organic periphery of the molecule. However, fragmentations also arise from cleavage of Si-O bonds, and from our studies we have found a combination of both types of bond cleavage.

The fragmentation patterns found for compounds of Type A are very similar and indicate a dissociative mechanism for all siloxanes irrespective of the nature of R, with the single exception of compound (24) where simple Me$^{\bullet}$ loss from the parent molecular ion was not seen.

Scheme 2.1

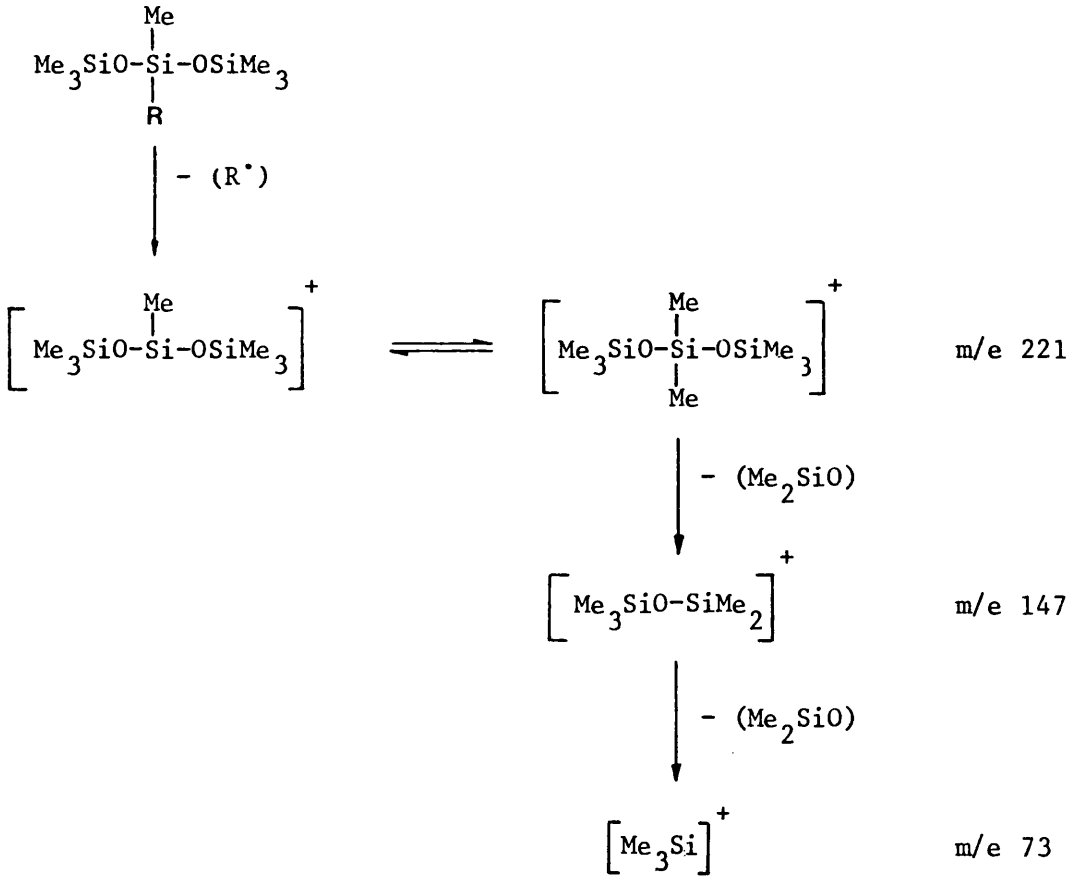


Table 2.10 E.I. mass spectra of $Me_3SiOSiMe(R)OSiMe_3$

Relative abundance of ions (base peak = 100)

	R	$(M)^+$	$(M - Me)^+$	$(M - R)^+$	$(M - R - CH_2)^+$	$(Me_2SiR)^+$	$(Me - 2Me)^{2+}$	$(Me_3SiOSiMe_2)^+$	$(Me_3Si)^+$	Others
(8)	$(CH_2)_2Ph$	4	20	100	38	3		2	38	
(10)	$(CH_2)_3Ph$	1	15	100	19	14		2	46	
(12)	$(CH_2)_3CN$	*	100	78	12	6	20	1	44	15(261) 48(246)
(15)	$(CH_2)_2C_6H_9$	*	8	100	22	2		10	38	
(17)	$CH{=}CH_2$	*	100	7	6	19	15	2	38	40(205)
(20)	$CH_2CH{=}CH_2$	*	38	100	8	15	6	4	75	15(205)
(24)	$(CH_2)_2Br$			65	25			18	100	60(287)
(26)	$(CH_2)_2PPh_2$	9	8	100	22	2	10	11	68	2(295) 3(247)
(30)	$(CH_2)_2SPh$	3	#	72	2			4	28	3(281) 100(149) 40(133)

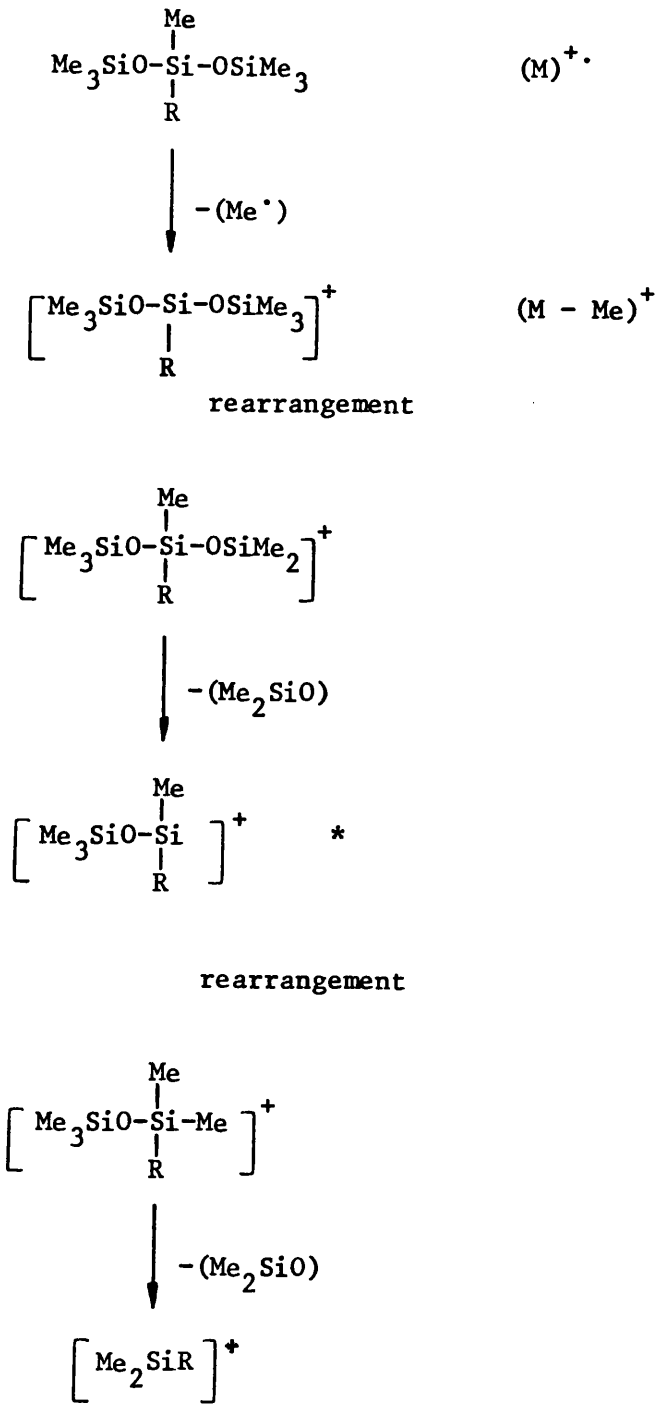
* no molecular ion detected in E.I. spectra, but $(M + H)^+$ clearly seen in C.I. spectra.

detected in C.I. spectrum.

Table 2.11 Mass spectra of $Me_3SiO\left[SiMe(R)O\right]_2SiMe_3$

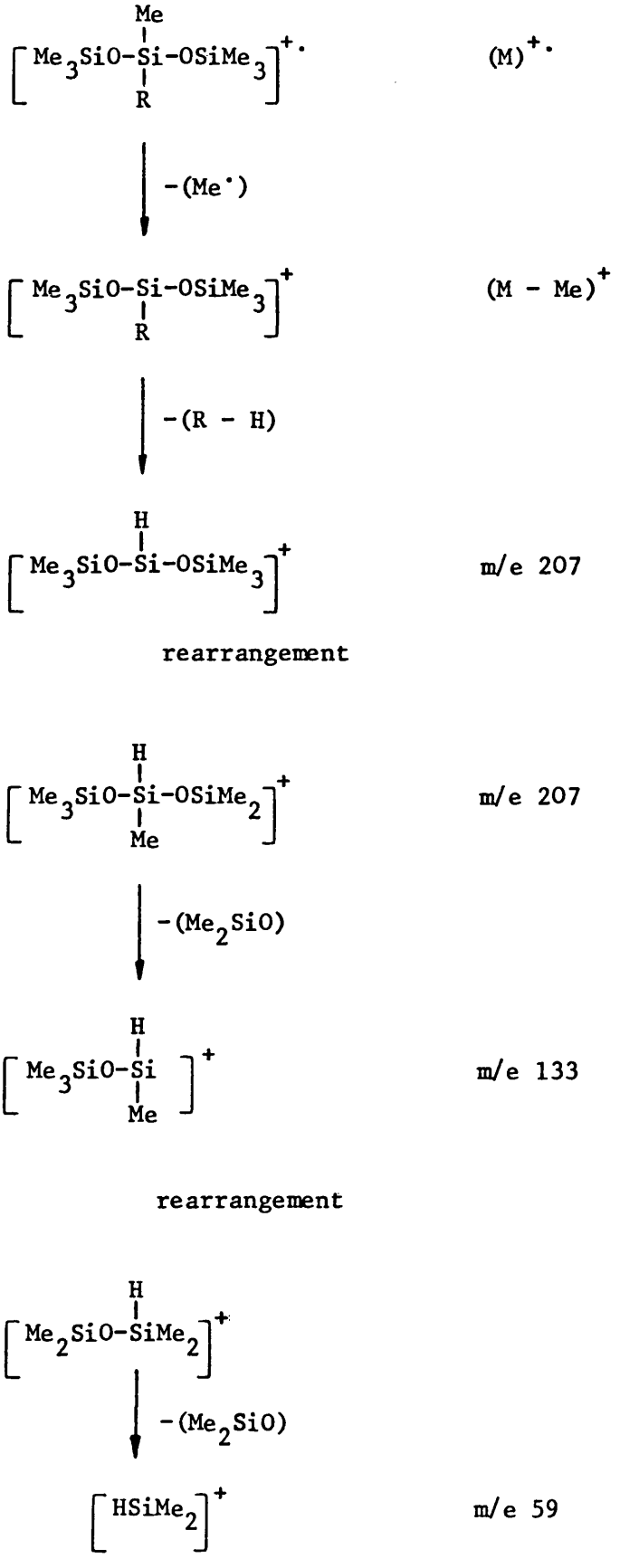
	Mode of ionisation	R	$(M)^+$	$(M+H)^+$	$(M-R)^+$	$(Me_2SiR)^+$	$(Me_3SiOSiMe_2)^+$	$(Me_3Si)^+$	$(M-Me)^+$	Others	
(9)	E.I.	$(CH_2)_2Ph$				5	9	49		19(311) 39(207)	100(221)
	C.I.			30	42	47	5	23	3	25(311) 18(207)	100(221) 47(163)
(3)	E.I.	$(CH_2)_3CN$			91	42	2	62	100	9(274) 22(98)	8(200)
	C.I.				2	1	2	2	1	16(327) 12(274)	10(290) 20(200)
(18)	E.I.	$CH=CH_2$			3	82	3	79	52	24(231)	
	C.I.			4	81		4		20	22(207)	38(109)
(27)	E.I.	$(CH_2)_2PPh_2$			2	1	9	88		24(262) 35(207)	100(221)
	C.I.			10	5	1	2	34	5	22(521) 11(221)	5(493) 17(207)

Scheme 2.2

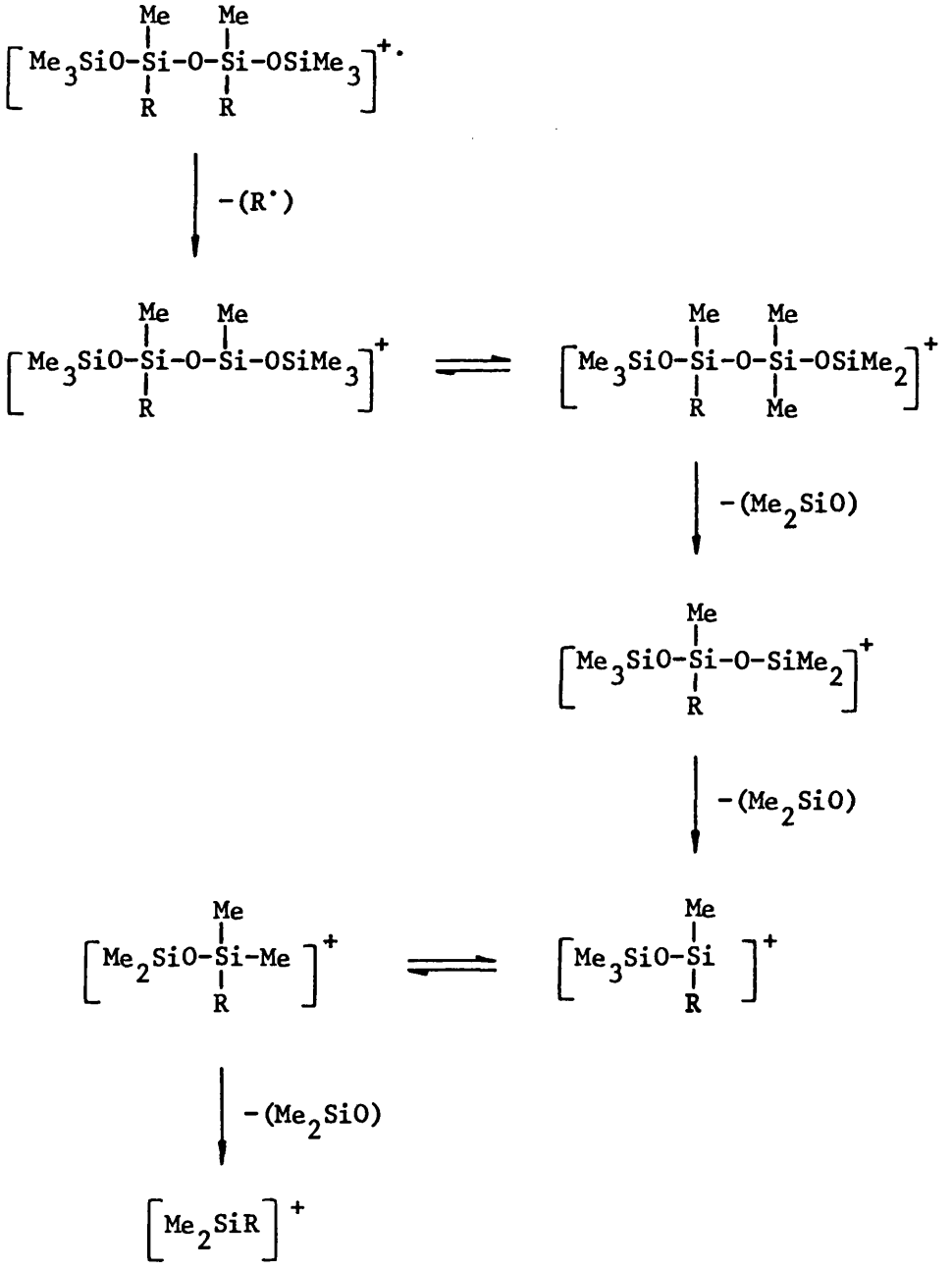


* only observed in C.I. spectra

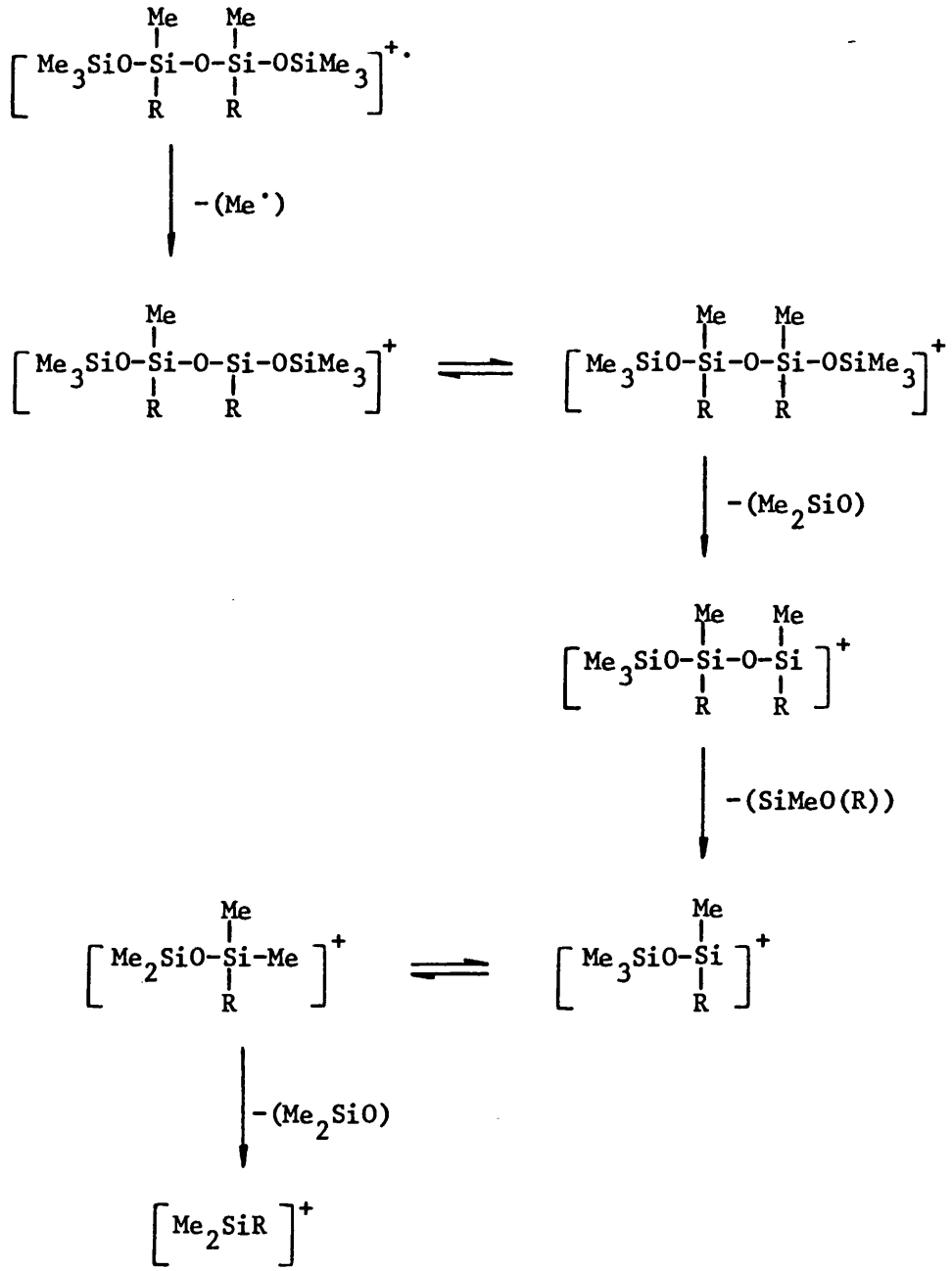
Scheme 2.3


Me
Me3SiO-Si-OSiMe3
R
(M)+·
-(Me·)
(M - Me)+
-(R - H)
H
m/e 207
rearrangement
H
Me3SiO-Si-OSiMe2
Me
m/e 207
-(Me2SiO)
H
Me3SiO-Si
Me
m/e 133
rearrangement
H
Me2SiO-SiMe2
-(Me2SiO)
HSiMe2
m/e 59

Scheme 2.4


Me
Me
Me3SiO-Si-O-Si-OSiMe3
R
R
+·
-(R·)
Me3SiO-Si-O-Si-OSiMe3
R
+
Me3SiO-Si-O-Si-OSiMe2
R
Me
-(Me2SiO)
Me3SiO-Si-O-SiMe2
R
-(Me2SiO)
Me2SiO-Si-Me
R
Me3SiO-Si
R
-(Me2SiO)
Me2SiR

Scheme 2.5



The formation of silanones ($R_2Si=O$) from siliconium ions is an important feature of the mass spectra of organosiloxanes, and these fragmentation species were first reported in 1980 by Swaim et al.[143] In the C.I., and to a lesser extent in the E.I. spectra, we too have frequently observed silanone ion elimination. For Scheme 2.1, after loss of the hydrocarbon group R from the parent ion $(M)^+$, to generate the intense ion fragment with m/e 221, two successive silanone eliminations give ions with m/e values of 147 and 73. Fragmentation Schemes 2.2 and 2.3 have the same initial step of methyl loss from the parent ion, i.e. $(M - Me)^+$. From this ion two disintegration routes are possible: the former scheme depicts a rearrangement whereby a methyl group from the trimethylsilyl moiety migrates to the central silicon atom, and is followed by silanone ion elimination. This rearrangement and elimination process is repeated to generate the ion $(Me_2SiR)^+$ which was found in the spectra of all compounds with the exception of compound (24). Alternatively, in Scheme 2.3, a second type of siliconium ion rearrangement can occur whereby a β-hydrogen from the alkyl side chain supporting the functional group migrates to the central silicon atom to form an Si-H bond. Simultaneously a neutral molecule containing an unsaturated carbon-carbon bond is eliminated. For compounds (8), (10), (12), (15), (17), (20), (24) and (26) the neutral molecules eliminated during this process would be styrene, allylbenzene, allylcyanide, 4-vinyl-1-cyclohexene, acetylene, propene, vinyl bromide and vinyldiphenylphosphine. From consideration of the relative intensities of fragment ions generated via Schemes 2.2 and 2.3, the former would appear more favoured for the trisiloxanes analysed.

Doubly charged ions have been observed previously in other studies on

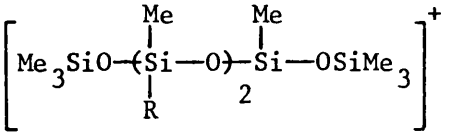
methylsiloxanes, and weak $(M - 2Me)^{2+}$ ions occur in the spectra of compounds (12), (17), (20) and (26). These ions correspond to the loss of two methyl groups from the molecular ion, and are identified on the spectrum by a cluster of closely spaced signals with the particular ion having a m/e value of (M - 30)/2.

Mass spectra have been recorded under C.I. and E.I. conditions for the following Type B compounds (9), (13), (18) and (28), and the main silicon containing ions together with their relative intensities are listed in Table 2.11. A number of similarities to the disintegrations of Type A compounds have been found with losses of hydrocarbon and siloxane fragments being observed. Generally the most intense ions found for Type A compounds were $(Me_3SiOSiMeOSiMe_3)^+$, $(Me_3SiOSiHOSiMe_3)^+$ and $(Me_3Si)^+$ at m/e values of 221, 207 and 73 respectively, and these fragments featured significantly in the spectra of Type B siloxanes. The C.I. spectra have proved to be more informative than E.I. spectra for analysing fragmentation routes from high mass ions, and the two sequences below (Schemes 2.4 and 2.5) illustrate general disintegration patterns. For compound (27), the peak found at m/e 521 corresponds to loss of the phosphine moiety ($-PPh_2$) from the molecular ion. A subsequent loss of ethene follows to give the ion at m/e 493. These fragmentations do not occur for the second R group since successive silanone ion loss appears to be a more favoured process (Scheme 2.4). The loss of a neutral unsaturated molecule by a siliconium ion rearrangement analogous to the mechanism shown in Scheme 2.3 does not feature significantly for Type (B) compounds.

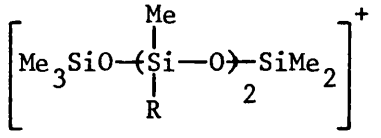
For Type (C) compounds, mass spectra were recorded for the nitrile (14) and vinyl (19) functionalised siloxanes.

On analysing the E.I. spectrum for compound (14), the fragmentation pattern

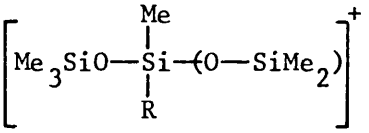
indicates a characteristic initial loss of a methyl radical from the molecular ion to give an ion peak at m/e 528 (22%). Subsequent losses of $H_2C{=}CHCN$, Me_2SiO and $H_2C{=}CHCN$ generate the intense ion peaks at m/e 475 (32%), 401 (96%) and 348 (100%) respectively. Structures for these ions are illustrated below.



m/e 475



m/e 401



m/e 348

The loss of vinylcyanide as opposed to allylcyanide from the Type (B) nitrile siloxane was the only significant difference found between the spectra of these compounds.

Further ion assignments are $(Me_3SiOSiMeH)^+$ at m/e 133 (24%), and those at m/e 207 and 73 which are commonly observed fragments in all our recorded spectra.

For compound (19) similar trends in the fragmentation pattern to its Type B analogue (18) were observed, and the assignments for the major ion peaks found in the C.I. spectrum are listed in Table 2.12.

Table 2.12 C.I. mass spectral data of $Me_3SiO\left[SiMe(R)O\right]_3SiMe_3$ (R = Vi)

Ion fragment	m/e	abundance (base peak = 100%)
$(M + H)^+$	421	1
$(M - Me)^+$	405	8
$(M - R)^+$	393	26
$(Me_3SiO(SiMeViO)_2SiMe_2)^+$	319	9
$(Me_3Si(SiHViO)(SiMe_2O)_2)^+$	293	12
$(Me_3SiO(SiMeViO)(SiMeH))^+$	219	9
$(Me_3SiOSiHOSiMe_3)^+$	207	10
$(Me_3SiOSiMeVi)^+$	159	7
$(Me_3SiOSiMe_2)^+$	147	6
$(Me_2SiR)^+$	85	45
$(Me_3Si)^+$	73	95

From our mass spectroscopy studies on functionalised siloxanes of Types (A), (B) and (C), we have found dissociation to follow pathways involving loss of methyl, hydrocarbon and siloxane fragments directly or through rearrangement processes for which we have proposed a number of fragmentation mechanisms based on experimental evidence.

2.5 EXPERIMENTAL PROCEDURES

Details of physical techniques and solvents appear in Appendices I and II respectively.

2.5.1 SYNTHESES OF FUNCTIONALISED CHLOROSILANES

$SiMeCl_2(CH_2CH_2Ph)$ (1).

Anhydrous $AlCl_3$ (0.36 g, 2.7 mmol) was added to a solution of dichloromethylvinylsilane (10.0 g, 70.9 mmol) in benzene (11.0 g, 0.14 mmol) and the mixture heated under reflux for 1h. After cooling to 0^oC, the mixture was filtered and the filtrate treated with NEt_3 (0.3 ml) in order to complex undissolved $AlCl_3$. A further small quantity of solid was removed by filtration and the filtrate distilled under reduced pressure, yielding compound (1) as a colourless oil (9.8 g, 63%), b.p. 89^oC (0.5 mmHg) (Found: C, 48.20; H, 5.60; Cl, 30.60. $C_9H_{12}Cl_2Si$ requires C, 49.30; H, 5.50; Cl, 32.40%).

$SiMeCl_2(CH_2CH_2CH_2Ph)$ (2).

This compound was prepared using the method of Musolf and Speier.[120] Allylbenzene (12.0 g, 1.0 mmol), dichloromethylsilane (9.7 g, 0.84 mmol) and 0.01 ml of 0.1 M chloroplatinic acid in isopropyl alcohol were heated to reflux for 5h. After cooling to ambient temperature, the mixture was distilled under reduced pressure, yielding compound (2) as a colourless oil (13.7 g, 70%), b.p. 88^oC (0.1 mmHg) (Found: C, 52.58; H, 6.14; Cl, 29.10. $C_{10}H_{14}Cl_2Si$ requires C, 51.50; H, 6.01; Cl, 30.47%).

$SiMeCl_2(CH_2CH_2CH_2CN)$ (3).

The title compound was prepared by the method of Speier *et al*.[121] Allyl cyanide (10.0 g, 149 mmol) and dichloromethylsilane (25.7 g, 223 mmol) were mixed and heated to reflux. To the refluxing mixture, three drops of 0.1 M chloroplatinic acid in isopropyl alcohol were added, and heating

was continued for 1h. Distillation of the mixture under reduced pressure gave (3) as a colourless oil (23.5 g, 86%), b.p. 94°C (2.3 mmHg) (Found: C, 32.98; H, 4.92; N, 7.72. $C_5H_9Cl_2NSi$ requires C, 32.96; H, 4.94; N, 7.69%).

$SiMeCl_2(CH_2CH_2C_6H_9)$ (4).

This compound was prepared using the method of the above stated authors.[121] 4-vinylcyclohexene (14.0 g, 130 mmol) with 1% platinum-carbon (2.7 mg) was heated to 120°C. Dichloromethylsilane (16.0 g, 140 mmol) was added dropwise such that the temperature did not fall below 105°C. Heating at this temperature was continued for 24h, before distillation of the mixture under reduced pressure yielded (4) as a colourless oil (21.5 g, 74%), b.p. 86°C (0.5 mmHg) (Found: C, 47.58; H, 7.30; Cl, 33.40. $C_9H_{16}Cl_2Si$ requires C, 48.43; H, 7.17; Cl, 31.8%).

$SiMeCl_2(CH_2CH_2Br)$. (5).

A slow stream of anhydrous HBr was passed through dichloromethylvinylsilane (12.0 g, 0.85 mmol) containing a catalytic quantity of benzoyl peroxide (0.1 g) at 0°C. The course of the reaction was monitored using infrared spectroscopy, following the dissappearance of the vinyl absorption at 1600 cm^{-1}. Fractionation under reduced pressure yielded compound (5) as a colourless oil (11.5 g, 61%) b.p. 45°C (2.9 mmHg) (Found: C, 15.50; H, 3.32. $C_3H_7BrCl_2Si$ requires C, 16.21; H, 3.15%).

$SiMeCl_2(CH_2CH_2PPh_2)$ (6).

The title compound was prepared using an adaption of the method of Brzezinska and Cullen.[88]

A mixture of dichloromethylvinylsilane (4.0 g, 28.4 mmol) and diphenylphosphine (5.27 g, 28.4 mmol) was sealed under a N_2 atmosphere in a

thick-walled Pyrex tube (25 cm^3). The tube was irradiated with light from a 400-W mercury lamp for 48h while the contents were continuously stirred. On completion of the reaction the product was isolated as a colourless, air-sensitive oil (8.80 g, 95%), b.p. 179°C (1.2 mmHg).

$SiMeCl_2(CH_2CH_2SPh)$ (7).

By using a similar procedure as above, this compound was isolated as an air-sensitive oil on irradiation of dichloromethylvinylsilane (4.0 g, 28.4 mmol) and thiophenol (3.26 g, 28.4 mmol) (6.7 g, 92%), b.p. 145°C (1.8 mmHg) (Found: C, 43.12; H, 4.79; S, 12.00. $C_9H_{12}Cl_2SSi$ requires C, 43.03; H, 4.78; S, 12.75).

2.5.2 SYNTHESES OF FUNCTIONALISED SILOXANES

$Me_3SiO(SiMe(CH_2CH_2Ph)O)_nSiMe_3$ (n = 1 or 2).

A solution of $SiMeCl_2(CH_2CH_2Ph)$ (10.2 g, 46.6 mmol) and $SiMe_3Cl$ (10.1 g, 93.2 mmol) in Et_2O (25 ml) was added dropwise with stirring to water (20 ml) cooled in ice. The stirred mixture was allowed to warm to ambient temperature over 1h. The ether layer was separated, dried, and the solvent removed in vacuo. Distillation of the residual oil under reduced pressure yielded compounds (8) and (9) as colourless oils (Table 2.13). Higher siloxanes remained undistilled.

By an analogous procedure using a 2:1 mole ratio of $SiMe_3Cl$ to dichlorosilane derivative, a range of siloxanes were produced ((10) - (23), Table 2.13).

Table 2.13 Analytical[a] data for siloxane derivatives

[a] calculated data in parentheses

[b] P/mmHg in parentheses

		n	Yield (%)	B.p.[b] (°C)	Analysis (%) C	H	N
(8)	$Me_3SiO\left[SiMe(CH_2CH_2Ph)O\right]_nSiMe_3$	1	33	116(0.1)	54.9(55.1)	9.16(9.20)	
(9)		2	24	198(0.8)	57.8(58.8)	8.65(8.57)	
(10)	$Me_3SiO\left[SiMe(CH_2CH_2CH_2Ph)O\right]_nSiMe_3$	1	57	106(0.1)	56.7(56.5)	8.89(9.40)	
(11)		2	19	192(0.2)	59.6(60.2)	8.82(8.88)	
(12)	$Me_3SiO\left[SiMe(CH_2CH_2CH_2CN)O\right]_nSiMe_3$	1	22	106(1.2)	44.5(45.5)	9.06(9.34)	
(13)		2	11	194(3.1)	45.4(46.2)	8.89(8.65)	
(14)		3	10	242(1.5)	46.5(46.4)	8.31(8.28)	7.73(7.73)
(15)	$Me_3SiO\left[SiMe(CH_2CH_2C_6H_9)O\right]_nSiMe_3$	1	50	92(0.2)	53.0(54.5)	10.50(10.30)	
(16)		2	23	172(0.2)	56.8(57.8)	10.40(10.00)	
(17)	$Me_3SiO\left[SiMe(CH=CH_2)O\right]_nSiMe_3$	1	12	46(1.2)	43.4(43.5)	9.32(9.67)	
(18)		2	40	82(1.3)	43.1(43.1)	8.84(8.98)	
(19)		3	32	97(1.3)	43.2(42.9)	8.76(8.57)	
(20)	$Me_3SiO\left[SiMe(CH_2CH=CH_2)O\right]_nSiMe_3$	1	36	29(0.1)	44.1(45.8)	9.96(9.92)	
(21)		2	8	54(0.01)	43.6(46.4)	9.70(9.39)	
(22)	$Me_3SiO\left[SiMe(H)O\right]_nSiMe_3$	1	28	38(12.0)	37.7(37.8)	10.07(9.90)	
(23)		2	39	74(12.0)	33.9(34.0)	9.19(9.22)	
(30)	$Me_3SiO\left[SiMe(CH_2CH_2SPh)O\right]_nSiMe_3$	1	46	159(1.8)	50.2(50.3)	7.93(8.38)	

$Me_3SiOSiMe(CH_2CH_2Br)OSiMe_3$ (24).

A slow stream of anhydrous HBr was passed through compound (17) (14.8 g, 59.6 mmol) containing a catalytic quantity of benzoyl peroxide (0.1 g). An exothermic reaction occurred and the temperature of the solution increased to 35 - 40°C. The reaction was assumed to be complete when the solution temperature returned to ambient. Fractionation under reduced pressure yielded compound (24) as a colourless oil (17.2 g, 88%), b.p. 74°C (1.3 mmHg) (Found: C, 33·10; H, 7.35; Br, 27.50. $C_9H_{25}BrO_2Si_3$ requires C, 32.80; H, 7.60; Br, 24.30%).

$Me_3SiOSiMe(CH_2CH_2CH_2C_5H_4N)OSiMe_3$ (25).

A solution of $LiCH_2C_5H_4N$ (7.78 g, 1.81 mmol) in thf (15 ml) was added dropwise with rapid stirring to a solution of compound (24) in thf (15 ml). The mixture was stirred for 3 days prior to distillation in the complete absence of oxygen. The product was isolated as a yellow, air-sensitive oil (4.70 g, 76%) b.p. 122°C (0.25 mmHg) (Found: C, 51.90; H, 9.20; N, 3.60. $C_{15}H_{31}NO_2Si_3$ requires C, 52.80; H, 9.10; N, 4.00%).

$Me_3SiOSiMe(CH_2CH_2PPh_2)OSiMe_3$ (26).

A mixture of compound (17) (4.00 g, 1.61 mmol) and $PHPh_2$ (2.50 g, 1.34 mmol) was sealed under a N_2 atmosphere in a thick-walled Pyrex tube (50 ml). The tube was irradiated with light from a 400-W mercury lamp for 48h while the contents were continuously stirred. On completion of the reaction the product was isolated as a colourless, air-sensitive oil (5.50 g, 79%) by distillation under reduced pressure b.p. 178°C (0.9 mmHg). (Found: C, 58.70; H, 8.00. $C_{21}H_{35}O_2PSi_3$ requires C, 58.1; H, 8.05%).

$Me_3SiO\left[SiMe(CH_2CH_2PPh_2)O\right]_2SiMe_3$ (27).

This compound was isolated as an air-sensitive oil in almost quantitative yield on irridation of (18) (1.72 g, 5.14 mmol) and $PHPh_2$ (1.91 g, 10.3 mmol) as above. Distillation without decomposition did not prove possible, but the oil appeared analytically pure after pumping in vacuo (0.01 mmHg) and there was no spectroscopic evidence for unreacted starting materials (Found: C, 60.4; H, 7.40; P, 8.60. $C_{36}H_{52}O_3P_2Si_4$ requires C, 61.20; H, 7.35; P, 8.80%).

$Me_3SiO\left[SiMe(CH_2CH_2PPh_2)O\right]_3SiMe_3$ (28).

This compound was prepared by a similar procedure to that used for (27) using (19) (2.0 g, 4.76 mmol) and $PHPh_2$ (2.65 g, 14.3 mmol). This product was isolated in almost quantitative yield as a colourless oil which appeared analytically pure from spectroscopic analysis. (Found: C, 61.30; H, 6.97; P, 9.61. $C_{51}H_{69}O_4P_3Si_5$ requires C, 62.57; H, 7.05; P, 9.51%).

$Me_3SiOSiMe(CH_2CH_2CH_2PPh_2)OSiMe_3$ (29).

This compound was prepared by an identical procedure to that used for (26), from (20) (2.00 g, 7.63 mmol) and $PHPh_2$ (1.18 g, 6.34 mmol), and was isolated as an air-sensitive, colourless oil (2.10 g, 58%), b.p. 190°C (0.1 mmHg) (Found: C, 59.60; H, 7.90. $C_{22}H_{37}O_2PSi_3$ requires C, 58.90; H, 8.25%).

2.5.3 SYNTHESES OF FUNCTIONALISED ORGANOSILANES

$Me_3SiCH_2CH_2Br$ (31).

The title compound was prepared by the literature method of Sommer et al.[119] Anhydrous HBr was passed through trimethylvinylsilane (12.0 g, 66 mmol) cooled to 0°C and containing a catalytic quantity of benzoyl peroxide (0.05 g). The reaction was monitored using infrared spectroscopy by following the vinyl group absorption. Fractionation of the mixture under reduced pressure yielded compound (31) as a colourless oil (16.6 g, 76%) b.p. 54°C (5.7 mmHg) (Found: C, 31.47; H, 7.16; Br, 43.51. $C_5H_{13}BrSi$ requires C, 33.15; H, 7.18; Br, 44.14%).

$Me_3SiCH_2CH_2PPh_2$ (32).

To a solution of $LiPPh_2$ (3.18 g, 16.6 mmol) in thf (10 ml) at 0°C was added dropwise with rapid stirring a solution of (31) in thf (2 ml). On addition, the red colouration was discharged to give a light green solution which was stirred for 1h at ambient temperature. The mixture was transferred to a N_2 filled distillation apparatus and fractionated under reduced pressure to yield the title compound as a colourless oil (2.1 g, 53%) b.p. 190°C (2.0 mmHg) (Found: C, 71.52; H, 8.24; P, 11.16. $C_{17}H_{23}PSi$ requires C, 71.32; H, 8.04; P, 10.83%).

Figure 2.1 Infrared spectrum of $(Me_3SiO)_2SiMe(H)$ (22)

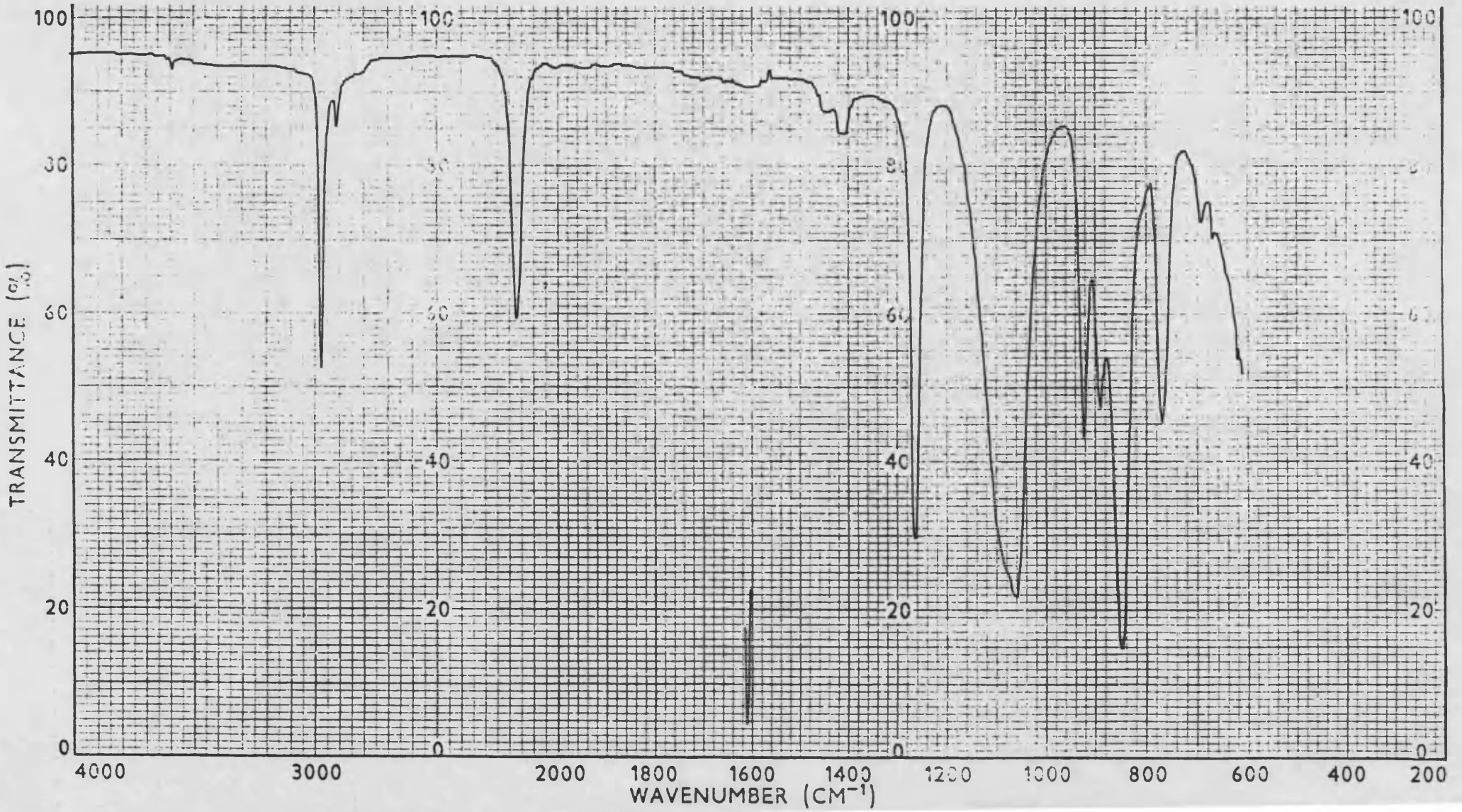


Figure 2.2 Infrared spectrum of $(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)$ (26)

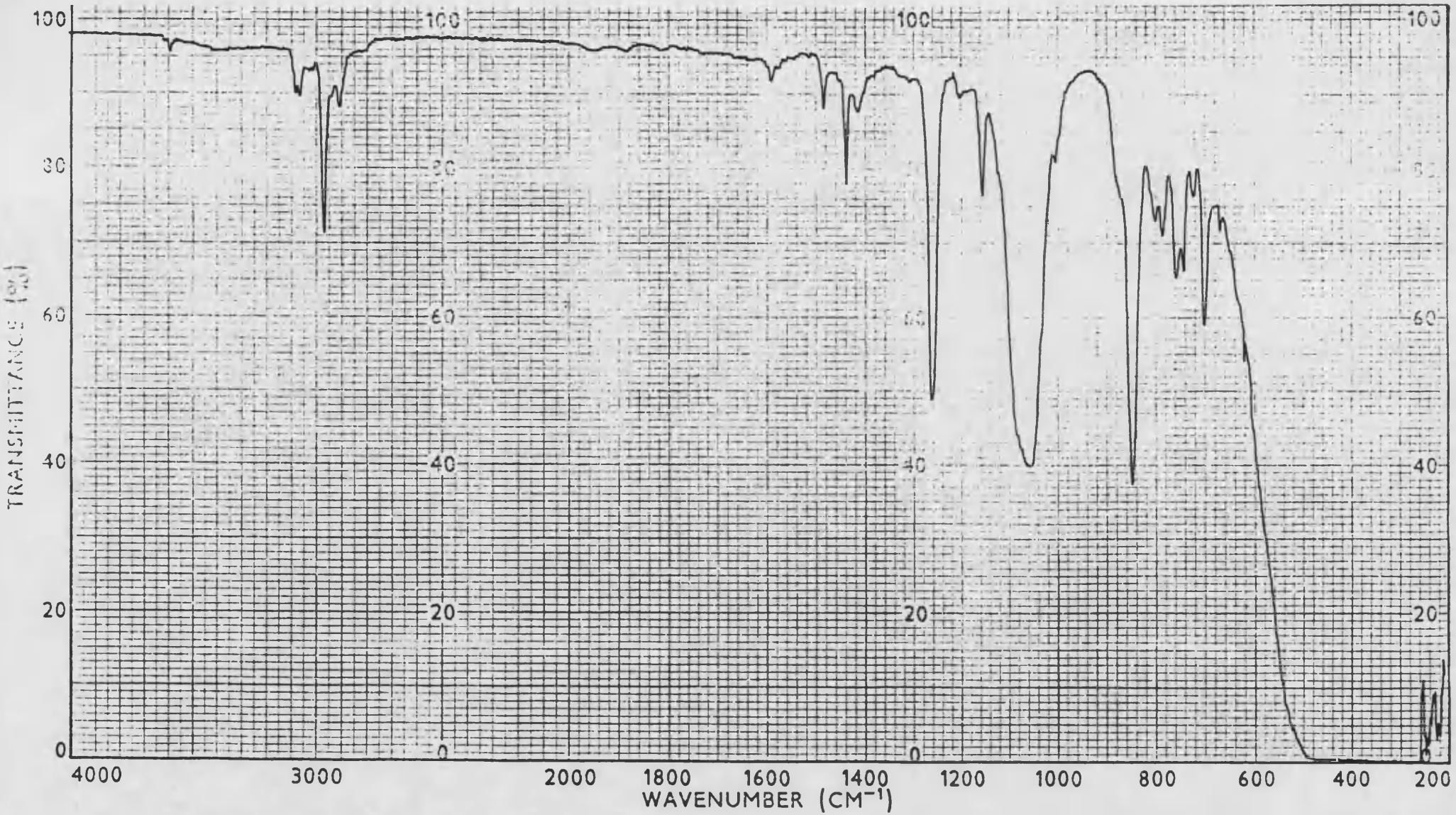


Figure 2.3 Infrared spectrum of $(Me_3SiO)_2SiMe(CH_2CH_2CH_2CN)$ (12)

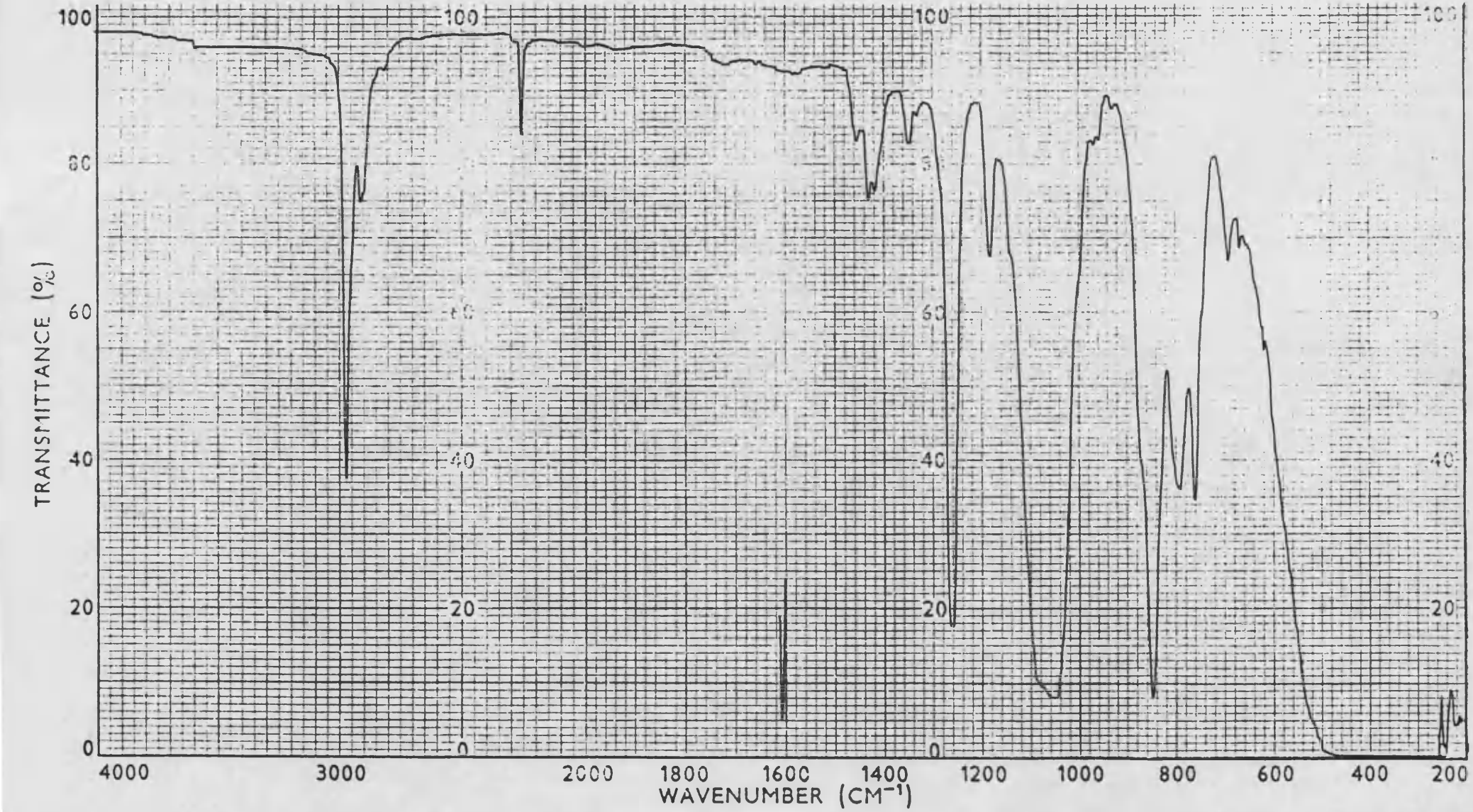


Figure 2.4 ^{13}C n.m.r. spectrum of $(Me_3SiO)_2SiMe(CH_2CH_2CH_2Ph)$ (10)

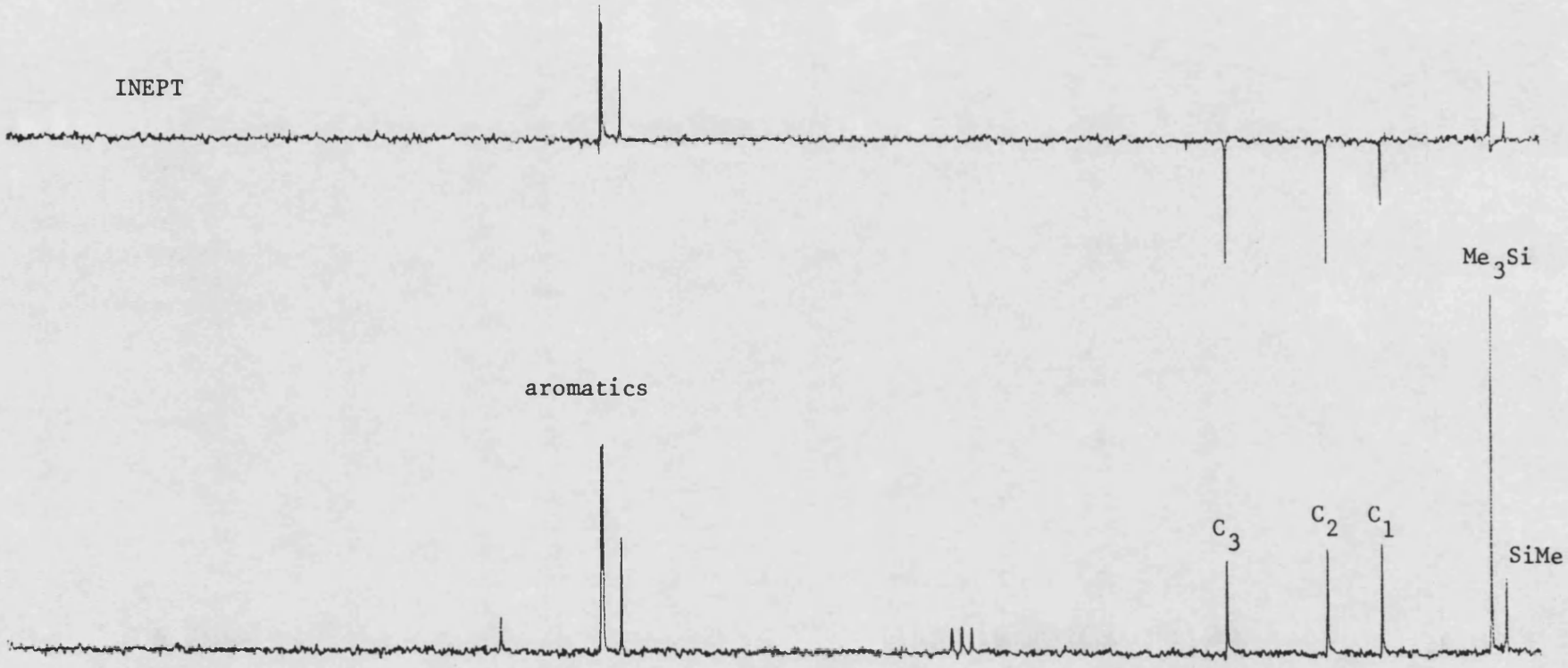


Figure 2.5 ^{13}C n.m.r. spectrum of $(Me_3SiO)_2SiMe(CH_2CH{=}CH_2)$ (20)

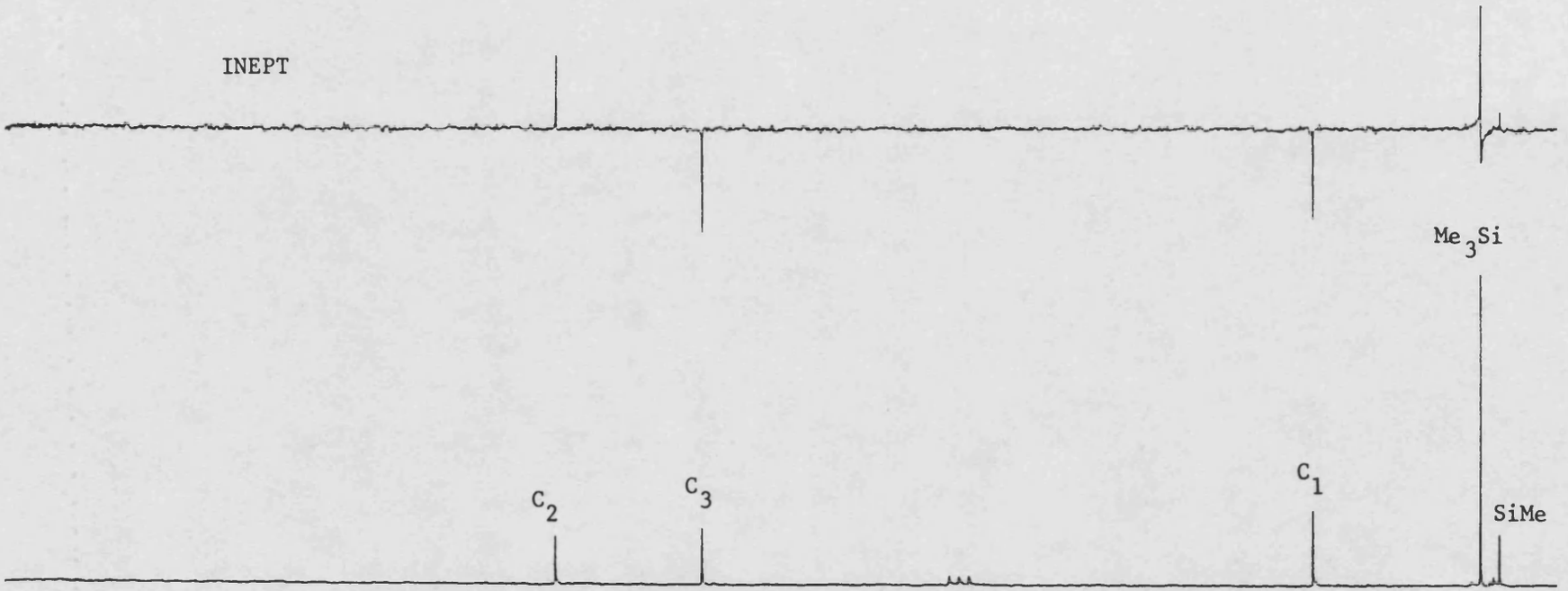
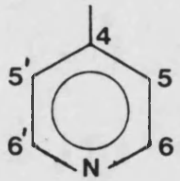


Figure 2.6 ^{13}C n.m.r. spectrum of $(Me_3SiO)_2SiMe(CH_2CH_2CH_2C_5H_4N)$ (25)



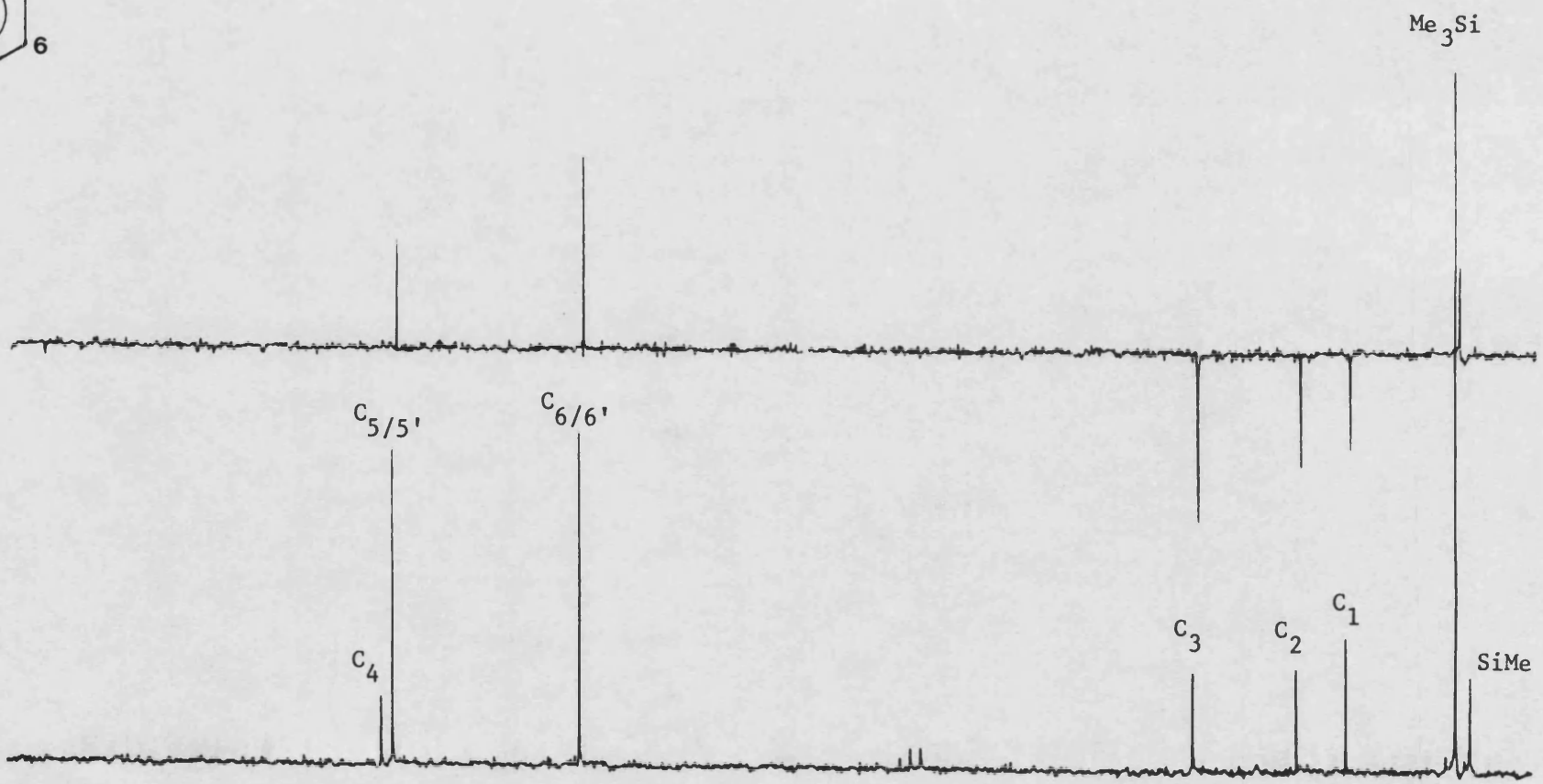


Figure 2.7 ^{13}C n.m.r. spectrum of $(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)$ (26)

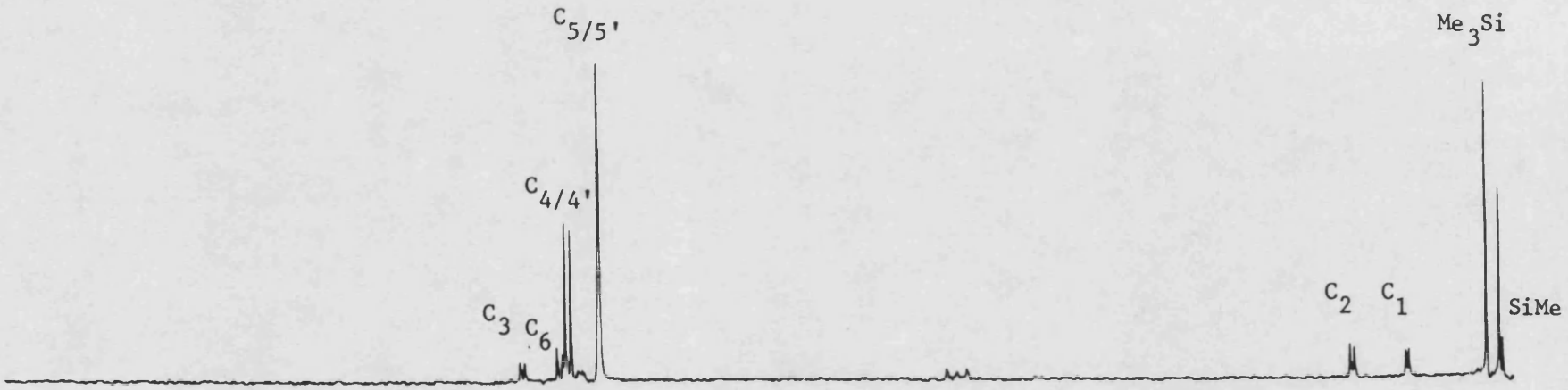
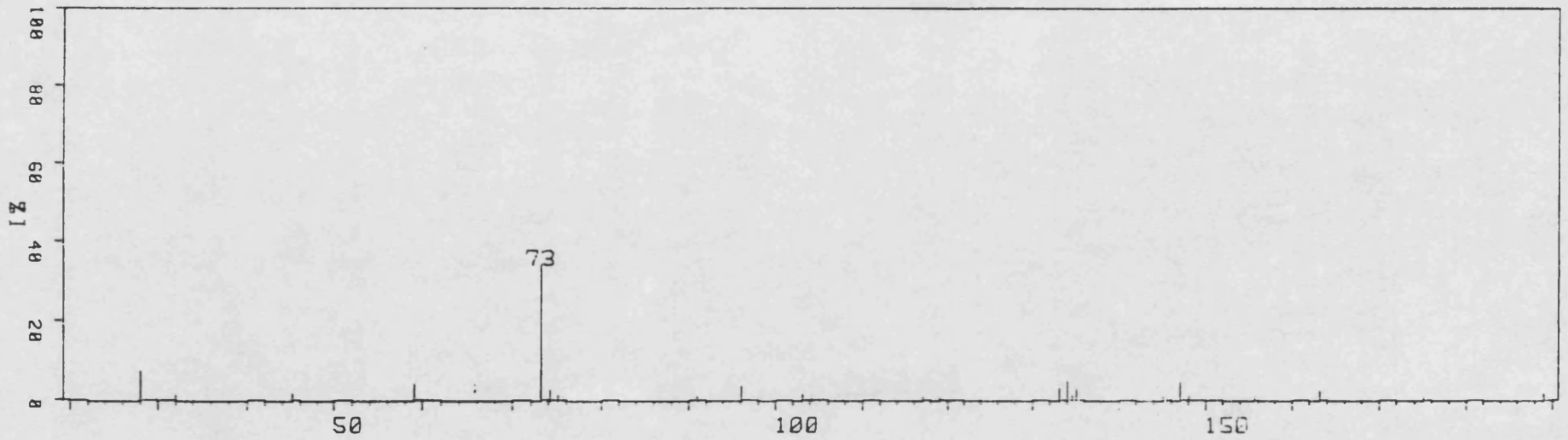


Figure 2.9 Mass spectrum of $(Me_3SiO)_2SiMe(CH_2CH_2Ph)$ (8)



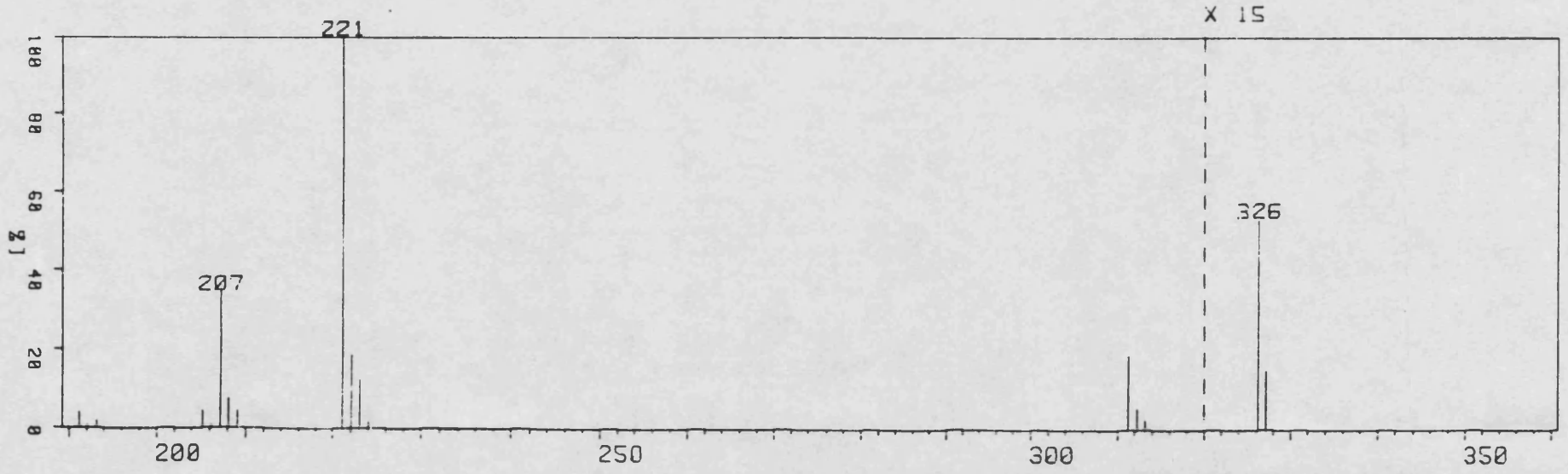
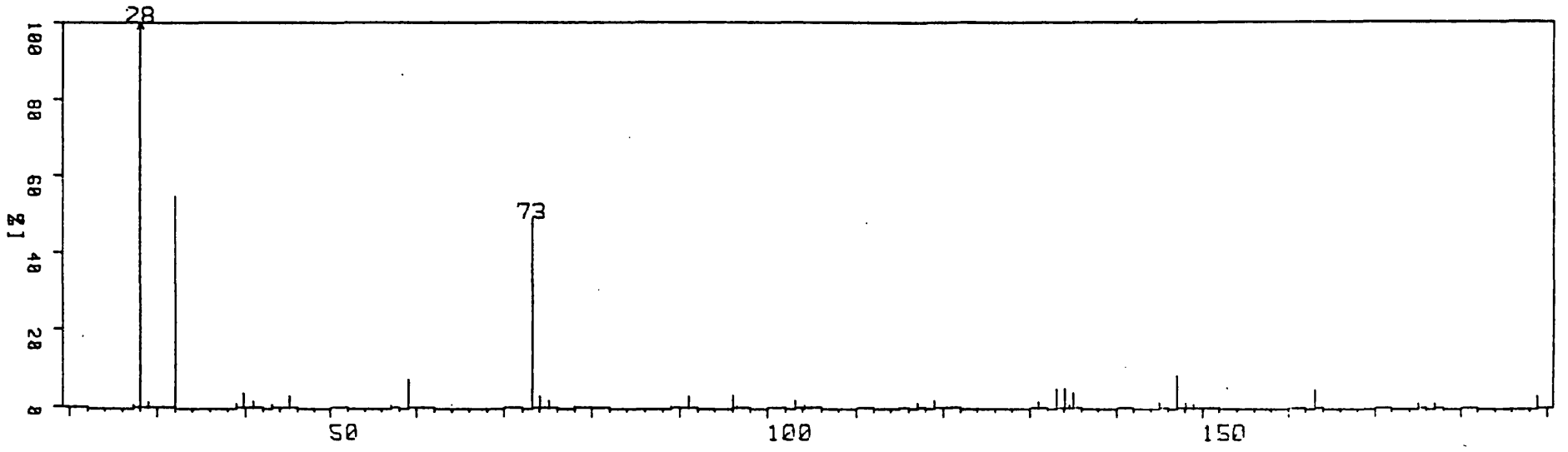


Figure 2.10 Mass spectrum of $Me_3SiO\left[SiMe(CH_2CH_2Ph)O\right]_2SiMe_3$ (9)



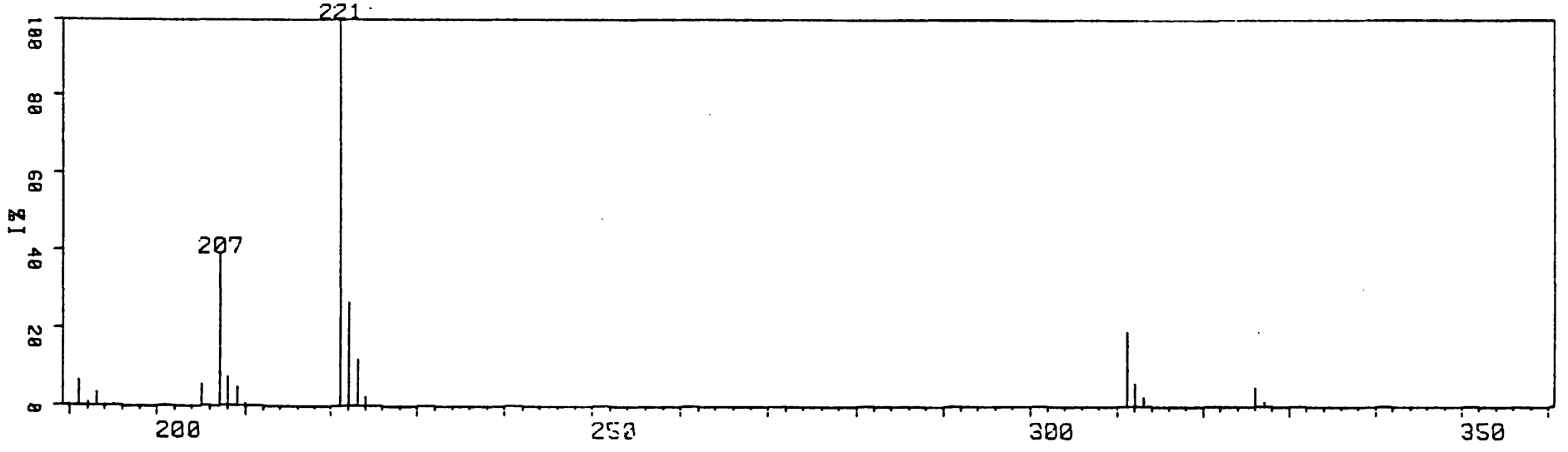


Figure 2.11 Mass spectrum of $(Me_3SiO)_2SiMe(CH_2CH_2CH_2CN)$ (12)

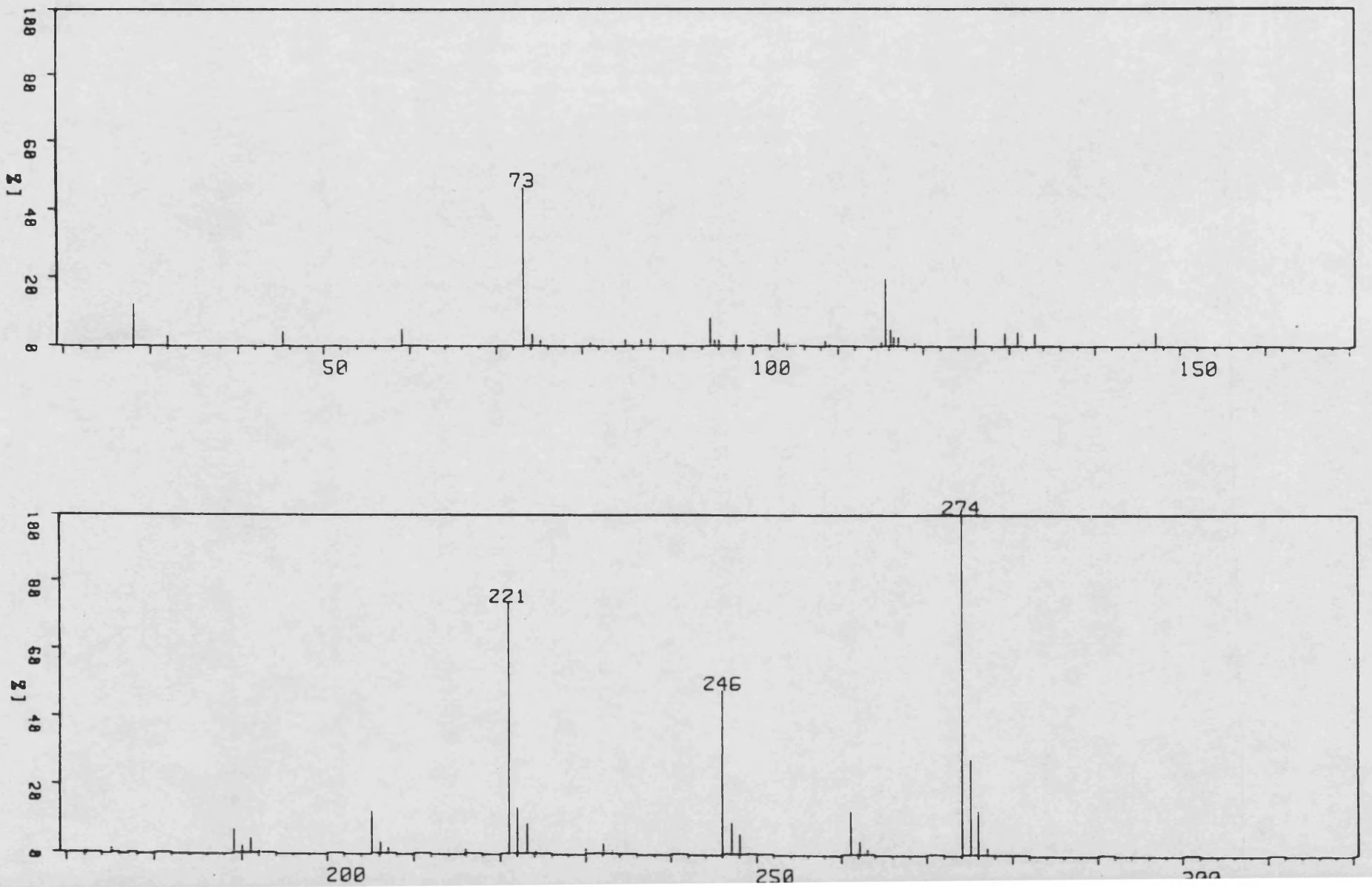


Figure 2.12 Mass spectrum of $Me_3SiO\left[SiMe(CH_2CH_2CH_2CN)O\right]_3SiMe_3$ (14)

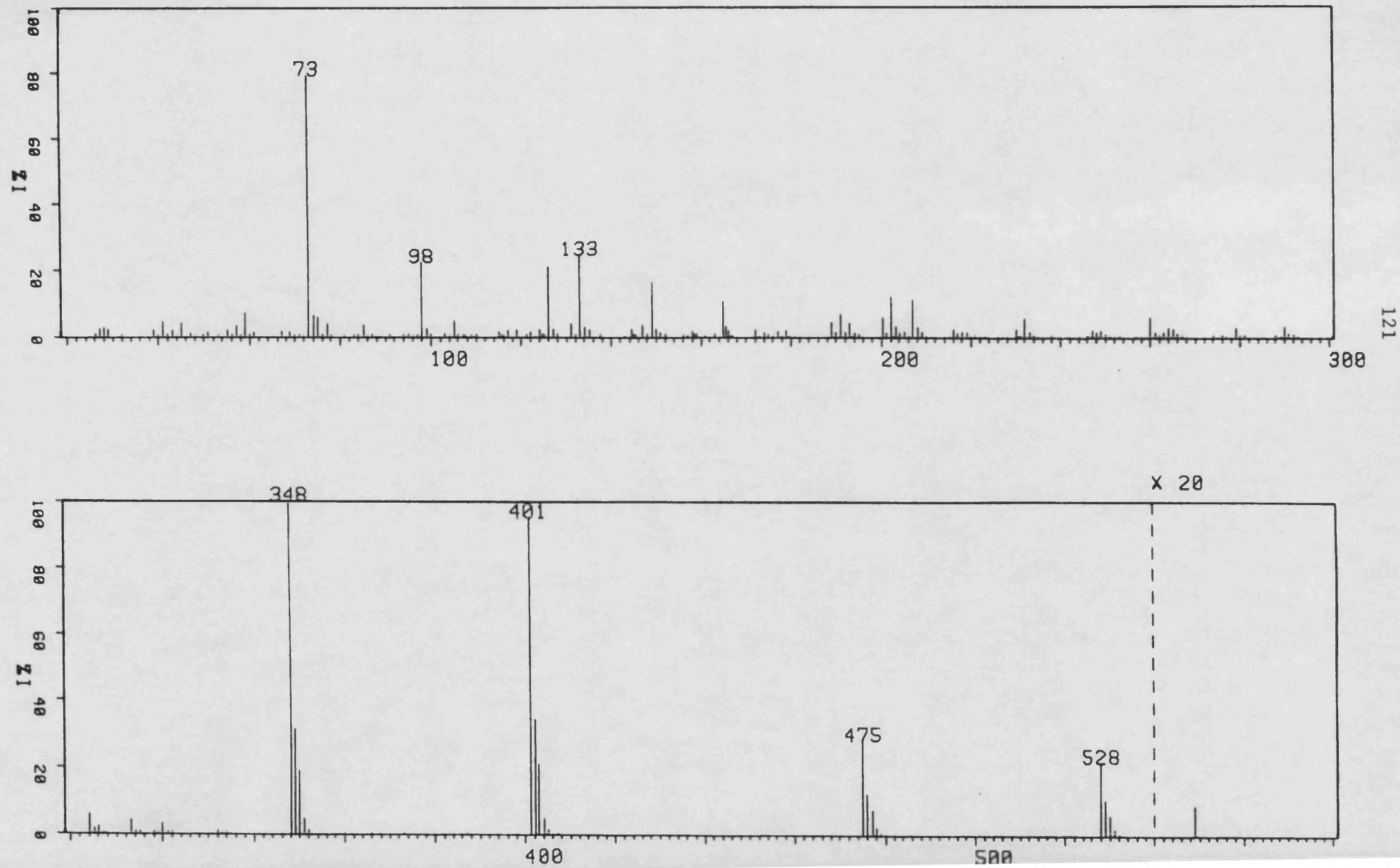
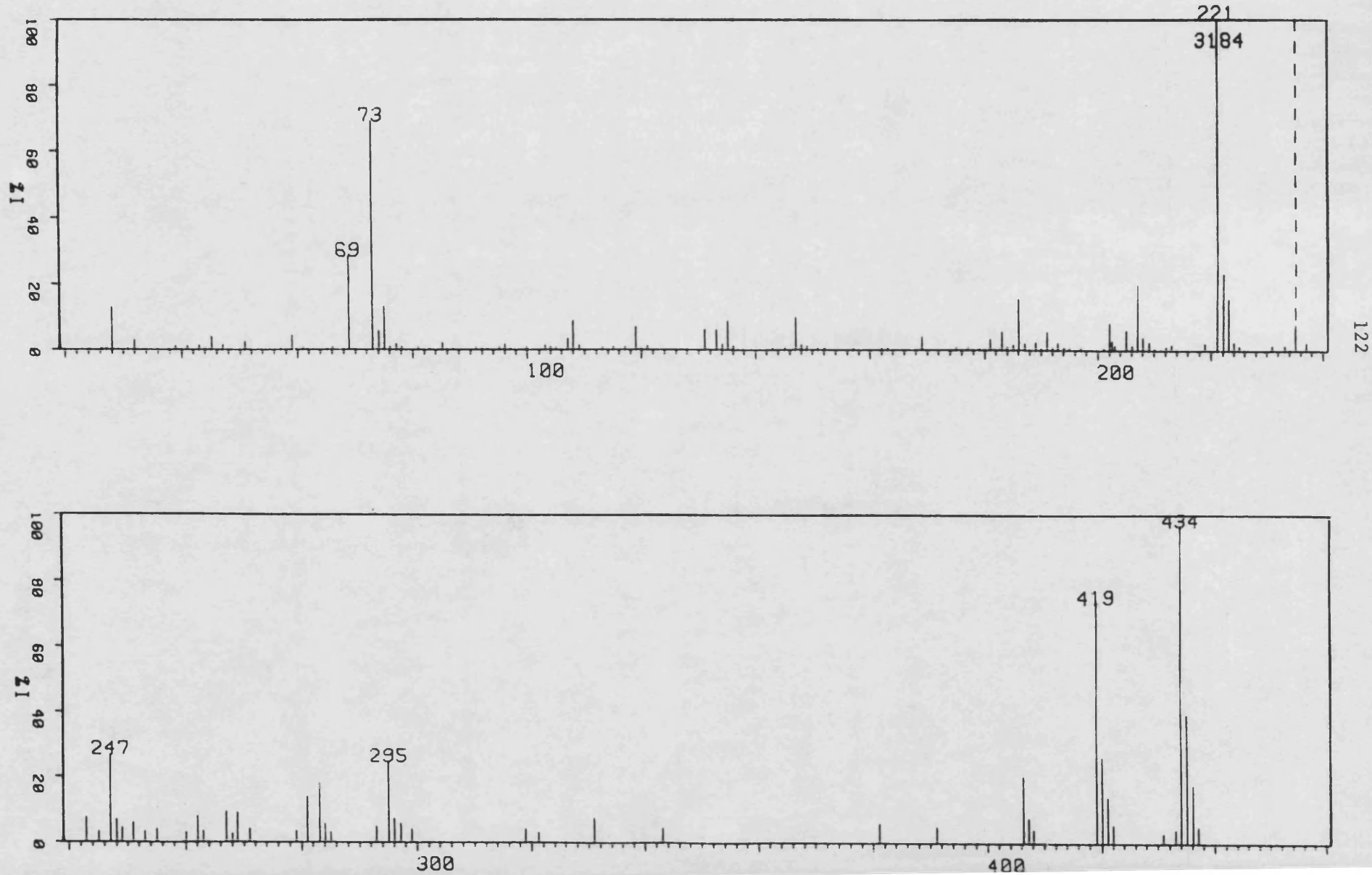


Figure 2.13 Mass spectrum of $(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)$ (26)



CHAPTER THREE

MODEL METAL COMPLEXED ORGANOSILOXANES

3.1 INTRODUCTION

From the range of model functionalised tri-, tetra- and penta- organosiloxanes prepared and listed in Chapter 2, we focused our attention on bonding a range of catalytically useful metal entities to many of these compounds. Polysiloxanes containing arene, phosphine, vinyl, nitrile, pyridine and allyl ligand endings have been successfully metallated, and the chemical and physical properties of the resulting materials form the subject of this chapter.

3.2 SYNTHETIC METHODS

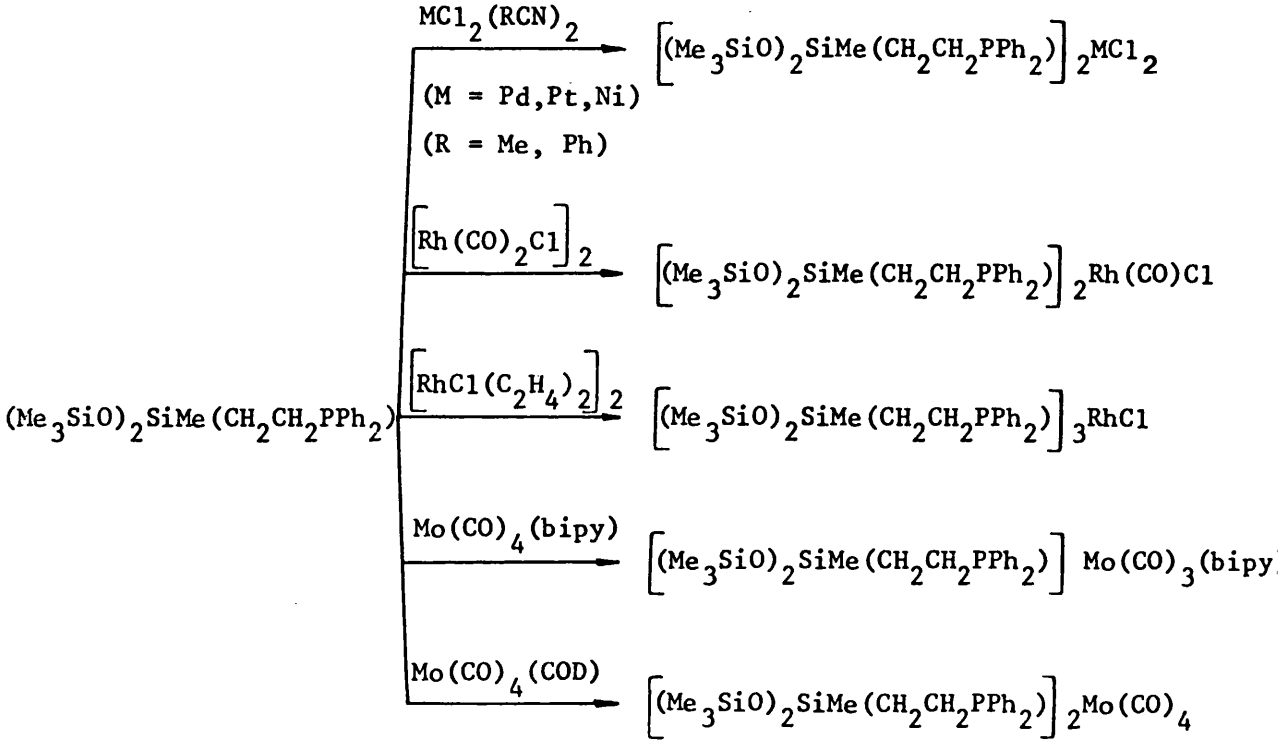
With the exception of two tetrasiloxane derivatives, all metal complexation reactions carried out employed the functionalised trisiloxanes (8), (10), (12), (17), (20), (25) and (26). The metals used in these reactions have included rhodium, palladium, platinum, nickel, molybdenum, chromium, iron and osmium, and the initial metal complexes used together with the anchored metal moieties derived from them are listed in Table 3.1. Table 3.2 lists formulae for the metallated siloxanes. All of the preparations and purification procedures were conducted under an inert atmosphere using absolute solvents and high purity starting materials. In many cases the metallated products proved to be very unstable and decomposition was evident even under a N_2 atmosphere. This frequently complicated characterisation procedures.

In view of the air and moisture sensitivity of the Si-Cl bond, our complexation reactions were carried out on organosiloxanes only, and not on any of the functionalised chlorosilanes (compounds (1) - (7)) which were described in Chapter 2. Although metal containing derivatives of these compounds could be prepared, the hydrolysis step to produce siloxane analogues may well lead to cleavage of Si-O linkages which are acid sensitive, or undesired chemical modification of the metal entity.

Furthermore, future syntheses of polysiloxane supported metal catalysts were not going to involve polymerisation of metallated chlorosilanes, and we wished to evolve general procedures which could be applied to these polymers.

Of the vast range of transition-metal entities which could be bonded to these functionalised siloxanes, we have selected metal halide and metal carbonyl derivatives. Such compounds are prominent in catalysis and provide representative examples on which to develop our synthetic strategies. The syntheses of compounds (31) - (46) have generally involved substitution reactions where groups within the reacting metal complex are easily displaced by the ligand functionalised siloxane under mild conditions. The most stable metallated derivatives prepared have proved to be those involving group VIII transition metals (Rh, Pd and Pt) in conjunction with phosphine functionalised siloxanes, and Scheme 3.1 illustrates examples using compound (26).

Scheme 3.1



The palladium, platinum and nickel halide compounds have been prepared by substitution of RCN (R = Me, Ph) from $MCl_2(RCN)_2$ under mild reaction conditions. Another synthetic approach has utilised bridge splitting in dimeric metal complexes. For example, two-electron donor ligands such as phosphines (L) can cleave rhodium-chlorine bridges in $\left[RhCl(C_2H_4)_2\right]_2$ with substitution of ethene to produce $RhCl(L)_3$ derivatives,[144] i.e.

Table 3.1 Anchored metal moieties derived from transition-metal complexes used in metallation reactions

Metal complex	Anchored metal moiety
$PdCl_2(PhCN)_2$	$PdCl_2$
$PtCl_2(MeCN)_2$	$PtCl_2$
$NiCl_2(MeCN)_2$	$NiCl_2$
$\left[Rh(CO)_2Cl\right]_2$	$Rh(CO)Cl$
$\left[RhCl(C_2H_4)_2\right]_2$	$RhCl$
$Mo(CO)_4(COD)$	$Mo(CO)_4$
$Mo(CO)_4(bipy)$	$Mo(CO)_3(bipy)$
$Mo(CO)_3(py)_3$	$Mo(CO)_3$
$Cr(CO)_6$	$Cr(CO)_3$
$\left[Rh(CO)_2Cl\right]_2$	$Rh(CO)_2Cl$
$Fe_2(CO)_9$	$Fe(CO)_4$
$H_2Os_3(CO)_{10}$	$H_2Os_3(CO)_{10}$

Table 3.2 Metallated organosiloxanes

(31) $\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]_2PdCl_2$

(32) $\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]_2PtCl_2$

(33) $\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]_2NiCl_2$

(34) $\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]_2Rh(CO)Cl$

(35) $\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]_3RhCl$

(36) $\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]_2Mo(CO)_4$

(37) $\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]Mo(CO)_3(bipy)$

(38) $\left[(Me_3SiO)_2SiMe(CH_2CH_2Ph)\right]Mo(CO)_3$

(39) $\left[(Me_3SiO)_2SiMe(CH_2CH_2Ph)\right]Cr(CO)_3$

(40) $\left[(Me_3SiO)_2SiMe(CH_2CH_2CH_2Ph)\right]Mo(CO)_3$

(41) $\left[(Me_3SiO)_2SiMe(CH_2CH_2CH_2C_5H_4N)\right]Rh(CO)_2Cl$

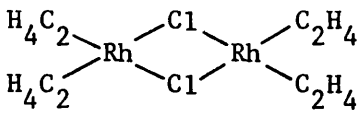
(42) $\left[(Me_3SiO)_2SiMe(CH_2CH_2CH_2C_5H_4N)\right]_2Mo(CO)_4$

(43) $\left[(Me_3SiO)_2SiMe(CH_2CH_2CH_2CN)\right]Rh(CO)_2Cl$

(44) $\left[(Me_3SiO)_2SiMe(CH{=}CH_2)\right]Fe(CO)_4$

(45) $\left[(Me_3SiO)_2SiMe(CH_2CH{=}CH_2)\right]Fe(CO)_4$

(46) $\left\{\left[(Me_3SiO\ SiMe(CH_2CH_2PPh_2)O\right]_2SiMe_2\right\}PdCl_2$



$$+ \quad 6L \longrightarrow 2\ RhCl(L)_3 \qquad (58)$$

The metal carbonyl containing compounds have all been prepared by substitution of carbon monoxide or other labile group(s) from a transition-metal carbonyl complex. For example, arene molybdenum tricarbonyl complexes have been synthesised by substitution of pyridine from $Mo(CO)_3(py)_3$ by arenes, and this method can be used for other group VI metals.[145]

More specifically, the palladium complexes (31) and (46) were synthesised in high yield by the reaction of the siloxyphosphines (26) and (27) respectively with $PdCl_2(PhCN)_2$ in acetone at ambient temperature. The platinum and nickel compounds (32) and (33) were prepared by reaction of $MCl_2(MeCN)_2$ with phosphine (26) dissolved in acetone and dichloromethane respectively.

The dimeric rhodium carbonyl complex $\left[Rh(CO)_2Cl\right]_2$ readily undergoes bridge splitting reactions with monomeric[144] and polymeric ligands (L) to produce complexes which have the general formula $Rh(CO)_2Cl(L)$. The nitrile (12) and pyridine (25) siloxanes, which both possess nitrogen donor atoms, have been reacted with the above carbonyl derivative to yield compounds (43) and (41) respectively. However, with tertiary phosphine ligands further substitution of carbon monoxide by a second phosphine occurs to give the complex $Rh(CO)Cl(L)_2$. We have prepared such a compound (34) where L = (26) using a similar method to that of Brzezinska and Cullen,[88] and have adopted

their synthetic procedure for the preparation of compound (35) by substitution of ethene in $\left[RhCl(C_2H_4)_2\right]_2$ by the siloxyphosphine (26).

The group VI metals chromium and molybdenum have both been used in complexation reactions. The tetracarbonyl molybdenum moiety $Mo(CO)_4$ was complexed to the phosphine (26) and pyridine (25) siloxanes by reaction with $Mo(CO)_4(COD)$ to produce compounds (36) and (42) respectively. Previous attempts to prepare compounds (36) and (42) by direct reaction of $Mo(CO)_6$ with the appropriate siloxanes in diglyme resulted in mixtures of tetra- and pentacarbonyl substitution products for both ligand types. A further carbonyl substitution reaction using the siloxyphosphine $(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)$ has been achieved with $Mo(CO)_4(bipy)$ to form compound (37), which was isolated as an air-stable solid after purification by column chromatography.

For the preparation of η^6-bonded $M(CO)_3$ (M = Cr, Mo) complexes with arene functionalised siloxanes, two methods have been employed. Firstly a thermal route involving reaction of $M(CO)_6$ with compounds (8) and (10) in various glyme/diglyme ether mixtures was tried, but only produced the desired complexes in low yields. This particular reaction, especially with chromium hexacarbonyl is believed to be hindered by a competing chain scission reaction where cleavage of Si-O linkages occurs. This has also been observed and reported by Pittman *et al*[85] for similar metal complexation studies on phenylsiloxane polymers. In our case, separation of the metallated siloxanes from high boiling solvents was also a complicating factor. A smoother complexation procedure at ambient temperature was found using $Mo(CO)_3(py)_3$ in the presence of boron trifluoride etherate. This method has been used by Nesmeyanov *et al*[145,146] to prepare $Mo(\eta^6\text{-arene})(CO)_3$ complexes. Boron trifluoride etherate serves to complex any liberated pyridine so yielding a complex which can

be easily removed by filtration. This route formed exclusively the $M(CO)_3$ complexed derivatives in yields of up to 60% in the case of molybdenum.

$$(Me_3SiO)_2SiMe(CH_2CH_2Ph) \xrightarrow[BF_3.OEt_2]{M(CO)_3(py)_3} \left[(Me_3SiO)_2SiMe(CH_2CH_2Ph)\right]M(CO)_3 \quad (59)$$

(M = Cr, Mo)

A similar procedure was adopted for the preparation of compound (40) from siloxane (10). For both chromium and molybdenum, the products were isolated as viscous yellow oils which rapidly decomposed on standing at ambient temperatures under an inert atmosphere.

The two iron tetracarbonyl complexes (44) and (45) have been prepared by reaction of iron nonacarbonyl with the vinyl(17) and allyl (20) functionalised trisiloxanes respectively. The reactions were both carried out in hexane at ambient temperature, with purification by column chromatography run under inert atmosphere conditions. The products were isolated as air/moisture sensitive yellow oils.

For the majority of preparative methods outlined above, separation of unreacted organosiloxanes from the metallated products has been readily achieved by column chromatography. This technique makes use of the relatively high R_f values of ligand functionalised siloxanes in non-polar solvents compared to their respective metallated derivatives. All of the metallated siloxanes had good solubilities in polar organic solvents such as acetone and dichloromethane.

In view of the instability of a number of the metallated siloxanes prepared in these studies, elemental analysis data could not be obtained for all complexes.

3.3 SPECTRAL CHARACTERISATION OF METALLATED ORGANOSILOXANES

The metallated trisiloxanes, compounds (31) to (45), have been characterised by infrared and nuclear magnetic resonance spectroscopes. On comparing each metallated compound to its non-metallated organosiloxane precursor, changes in absorption frequency and nuclear magnetic resonance shifts (^{1}H and ^{13}C) were found to be greatest for those atoms or groups involved at the anchor site, whilst the trisiloxane backbone, $Me_3SiOSiMeOSiMe_3$, was relatively unchanged. Both forms of spectral measurement yielded distinguishable signals for this specific section of both the metal moiety and anchoring ligand.

3.2.1 INFRARED SPECTROSCOPY

The infrared spectra of metallated organosiloxanes have been measured as either neat samples or as nujol mulls held between NaCl discs, and the results have been used for the qualitative analysis of functional groups and supported metallic moieties.

Transition-metal carbonyl complexes have been used extensively in anchoring reactions to both polymeric and solid supports, and in many cases produce active catalysts suitable for olefin metathesis,[147] isomerisation[148] and hydroformylation.[149] Transition-metal carbonyl complexes normally give rise to strong absorption bands in their infrared spectra, and the course of reactions involving such complexes can be followed easily and quickly by monitoring the increase or decrease in the intensities of specific bands using this technique. The carbonyl absorptions of many of our products

(listed in Table 3.3.) are structurally diagnostic, and assignments have been made by comparison with similar metal containing compounds, including both discrete molecules and polymer/solid supported analogues.[17,51]

A noteable feature of the infrared spectrum of compound (34) is a single intense absorption at 1965 cm^{-1} for the single carbonyl group. This observation is in general agreement with those findings of Brzezinska and Cullen,[88] and of other workers[150] for similar <u>trans</u>- $Rh(CO)Cl(L)_2$ (L = tertiary phosphine) complexes, where the two phosphine ligands are equivalent. For a <u>cis</u>-configuration of the ligands, a single carbonyl absorption would be anticipated at approximately 1980 cm^{-1}.[151] The (Rh-Cl) stretch expected for (34) in the far infrared region of the spectrum was not observed owing to masking by other absorptions.

For compounds (41) and (43) of general formula <u>cis</u>-$Rh(CO)_2Cl(L)$ (L = (12) or (25)), a pair of strong, sharp carbonyl absorptions at 2095/2025 and 2085/2025 cm^{-1} respectively were seen. These values are consistent with those reported for other <u>cis</u>-$Rh(CO)_2Cl(L)$ complexes, including the homogeneous pyridine analogue,[144] and for analogous silica anchored derivatives.[50] The change in absorption frequency for the (C≡N) stretch of compound (12) on complexation with $\left[Rh(CO)_2Cl\right]_2$ (<u>ca</u> 50 cm^{-1}), represents a shift towards the long wavelength region of the spectrum. In the case of the pyridine ligand, a much smaller change in the C=N stretching mode was found on complexation (from 1602 - 1612 cm^{-1}).

The molybdenum (38) and chromium (39) η^6-tricarbonyl complexed arene functionalised siloxanes each show two intense carbonyl absorptions at 1973/1894 and 1970/1893 cm^{-1} respectively. These bands, especially for the chromium analogue, are in good agreement with those found for chromium complexed arenesiloxane polymers prepared by Awl <u>et al</u>[86] and by Pittman <u>et al</u>[85] using similar synthetic procedures.

Table 3.3 Infrared carbonyl absorption data for selected metallated organosiloxanes

Compound	Representations for CO stretches	Number of IR active frequencies	$(C\equiv O)^a (cm^{-1})$
34[b]	A_1	1	1965s
36[b]	$2A_1 + B_1 + B_2$	4	2026s, 1953m, 1925s, 1896s
38	$A_1 + E$	2	1973s, 1894s
39	$A_1 + E$	2	1970s, 1893s
41	$A' + A''$	2	2085s, 2025s
42	$2A_1 + B_1 + B_2$	4	2020s, 1940s, 1885s, 1840s
45	$2A_1 + B_1 + B_2$	4	2080s, 2005s, 1975s, 1950m

a measured as neat sample

b measured as nujol mull

The carbonyl absorptions for compounds (36) and (42) $Mo(CO)_4L_2$ were very similar with four bands being observed between 2026 and 1840 cm^{-1}. This is indicative of a cis-arrangement for the two organosiloxane ligands (L), and an overall effective C_{2v} symmetry for the molecule.[152]

The iron tetracarbonyl π-complexes of vinylsiloxane (17) and the allylsiloxane (20), compounds (44) and (45) respectively, produce the greatest

changes in absorption frequency for the ligand groups on complexation. For compound (44), the shift of the (C=C) bond towards the long wavelength region of the spectrum was in excess of 270 cm^{-1}, and for the analogous allylic (C=C) band in (45) a change of 208 cm^{-1} was observed. Shifts of this magnitude have been reported by Rybinskaya et al[96] in their studies on iron carbonyl π-complexes of vinylsilanes. The carbonyl absorptions for (44) are at 2088, 2062, 2009 and 1983 cm^{-1} and indicate that one equatorial CO group in the trigonal bipyramidal $Fe(CO)_5$ molecule has undergone substitution by the vinylsiloxane.

For the series $\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]_2MCl_2$ (where M = Pd, Pt and Ni for compounds (31) - (33) respectively) far infrared spectra were recorded to identify metal-chlorine stretching vibrations, and comparisons to literature reports have shown the ligands to be in a trans-configuration. In each case, although the absorption intensities were relatively weak, they were sufficiently distinct from other vibrations for assignments to be made. For compounds (31) and (32), (Pd-Cl) and (Pt-Cl) stretches were at 351 and 342 cm^{-1} respectively and are in close agreement with the corresponding absorptions observed by Bruner and Bailar[153] in palladium and platinum dichloride complexes supported on diphenylphosphine functionalised Amberlite, and from results reported by Andersson and Larsson[154] on polymer bound palladiumphosphine complexes. Adams et al[155] have recorded the far infrared spectra of numerous square-planar platinum complexes (PtX_2L_2 X = Cl or Br) and found the (Pt-Cl) stretch to be almost insensitive to L when the ligands are in a trans-configuration, with an absorption range of 339.5 ± 3.1 cm^{-1}. For the analogous nickel complex (33) we have assigned a medium intensity band at 400 cm^{-1} to the (Ni-Cl) stretching, which is based on earlier studies by Nakamoto and co-workers[156,157] on $Ni(PR_2R')X_2$ complexes. A weak band at 248 cm^{-1}

found in the spectrum of (33) was the only identifiable example of (M-P) stretching. The (Rh-Cl) stretch in compound (35) was observed as a very weak absorption at 261 cm^{-1} which is in agreement with literature data.[88]

In compounds (31) - (37) and (46), the metal complexes are anchored through a diphenylphosphine group, and for spectra recorded as nujol mulls or neat samples there were no significant changes in absorption frequencies for the aromatic (C=C) skeletal stretches. Similarly, no outstanding changes were noted for aromatic (P-C) stretching expected in the range 1450 - 1435 cm^{-1} on complexation reactions of compound (26).

3.3.2 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

^{1}H and ^{13}C n.m.r. spectra have been recorded for compounds (31) to (45) with the exception of (33) (which decomposed rapidly in solution) in order to corroborate other structural data and to obtain information on coupling constants. Spectral results are summarised in Table 3.4 with representative ^{13}C spectra (Figures 3.1 - 3.6) illustrated for compounds (31), (34), (35), (41), (43) and (45) respectively. All of the prepared samples had good solubility in deuterated solvents, and high sample concentrations were frequently used for ^{13}C n.m.r. studies to enable detection of metal carbonyl resonances. A number of compounds decomposed during the accumulation of spectral data and consequently in some spectra signals were observed for both the free and metal complexed siloxane. Comparism of the ^{1}H and ^{13}C n.m.r. data of metallated and non-metallated organosiloxanes revealed that shift differences δ(shift) = δ(complexed) - δ(free) were greatest for those ligand endings involved in direct bonding to the metal complex, with δ(shift) values diminishing with increasing distance from the metal centre.

Table 3.4 1H and 13C n.m.r. data for selected metallated organosiloxanes

	OSiMe	SiMe	C1/H1	C2/H2	C3/H3	OTHERS	AROMATICS
(31)	0.02(36H, s) 1.81	0.04(6H, s) -0.68	0.58(4H, m) 11.81	2.22(4H, m) 19.20(13.42)			7.56(m) & 7.82(m) (total 20H) 126.77, 123.33(d, 45.2), 123.14, 121.03(t, 9.77)
(32)	0.00(36H, s) 1.70	-0.06(6H, s) -0.74	0.55(4H, m) 12.16	2.34(4H, m) 25.64			7.34(20H, m) 133.50(t, 4.88), 130.63, 128.03(t, 4.88)
(34)	0.12(36H, s) 2.34	0.12(6H, s) 0.32	1.02(4H, m) 12.80	2.88(4H, m) 22.03		188.6(73.24)(CO)	7.08(12H, m), 7.92(8H, m) 135.89, 134.91, 134.46, 134.20, 133.94, 130.23, 128.93, 128.74, 128.48
(35)	0.20(54H, s) 1.54	0.17(6H, s) -1.00	0.80(6H, m) 7.44(7.0)	2.32(6H, m) 19.64(70.3)			7.40(m) & 7.68(m) (total 30H) 134.86, 131.28(d, 2.44), 130.57(d, 9.77), 128.27(d, 10.98)
(36)	0.02(36H, s) 1.81	0.02(6H, s) -0.53	0.40(4H, m) 11.23	2.42(4H, m) 27.74		211.2(CO)	7.31(20H, m) 139.58(16.1), 136.66(14.0), 132.17, 128.14
(37)	0.00(18H, s) 2.40	0.06(3H, s) 0.45	0.43(2H, m) 12.02	2.00(2H, m) 24.89		7.28-8.92(8H, m) 155.40, 152.98, 137.51, 126.14, 123.54, 229.5(CO)	7.15(10H, m) 135.82, 133.45(10.2), 131.47, 129.39(8.8)
(38)	0.14(18H, s) 2.45	0.14(3H, s) 0.37	0.78(2H, m) 19.93	2.46(2H, m) 29.42	222.6(CO)	5.42(5H, m) 96.04, 94.35, 93.76, 91.81	7.20(5H, m) 135.40, 129.55, 128.95, 126.30
(39)	0.14(18H, s)	0.05(3H, s)	0.56(2H, m)	2.30(2H, m)		4.50(5H, m)	
(40)	0.18(18H, s) 2.06	0.12(3H, s) 0.00	0.44(2H, m) 17.61	1.42(2H, m) 25.68	2.00(2H, m) 38.46		4.72(5H, m) 95.18, 93.88, 91.55
(41)	0.18(18H, s) 2.06	0.18(3H, s) 0.00	0.44(2H, m) 17.55	1.48(2H, m) 23.84	2.22(2H, m) 38.41	183.33(68.36)(CO)	6.60(2H, m), 8.34(2H, m) 155.32, 152.07, 125.36
(42)	0.07(36H, s) 1.55	0.07(6H, s) -0.60	0.46(4H, m) 16.95	1.61(4H, m) 23.52	2.62(4H, t) 38.00	205.7(CO)	7.04(4H, m), 8.46(4H, m) 153.10, 149.30, 124.44
(43)	0.12(18H, s) 2.14	0.12(3H, s) 0.00	0.38(2H, m) 17.22	1.30(2H, m) 19.89	1.76(2H, t) 20.60	123.35(CN), 180.4(73.24)(CO)	
(44)	0.18(18H, s) 1.88	0.24(3H, s) 1.62	2.62(1H, m) 41.85	1.83(2H, m) 40.36		211.7(CO)	
(45)	0.25(18H, s) 0.22	0.34(3H, s) -0.22	1.77(2H, d) 25.03	3.60(1H, m) 61.60	2.00(2H, m) 48.38	210.7(CO)	

The ^{1}H n.m.r. spectrum for the rhodium carbonyl compound (34) has been reported previously,[88] and we have extended the spectral characterisation of this metallated siloxane with ^{13}C n.m.r. data. Coupling of the ^{31}P nucleus with both the aromatic carbons and the methylene group adjacent to phosphorus centre is evident with complex splitting patterns being observed. However, only for C_2 has a coupling constant (13.18 Hz) been accurately measured. The single carbonyl group resonates as a doublet centred at δ 188.6 with $J(^{103}Rh-^{13}C)$ coupling of 73.24 Hz, which is consistent for a planar trans-configuration for this complex. Similarly, for the rhodium-pyridine (41) and -nitrile (43) complexes the carbonyl signals were observed as doublets at δ 183.33 and 180.4 with coupling constants of 68.36 and 73.24 Hz respectively. To date, ^{13}C spectral parameters have only been reported for two $Rh(CO)_2Cl(L)$ complexes[158] (L = pyridine or piperidine), with the number of signals in the metal carbonyl region being dependent on the temperature at which the spectra were recorded. At $-60^{o}C$, for $Rh(CO)_2Cl(py)$, the authors observed a fairly sharp doublet of doublets which indicated the non-equivalence of carbonyl groups within the adduct. However, on warming to ambient temperature a sharp doublet at δ 183.1 with $J(^{103}Rh-^{13}C)$ = 69.9 Hz was found. For the retention of Rh-C coupling, the authors believed a fast ligand exchange process was occurring involving the pyridine group only. We have only recorded spectra at ambient temperature for (41) and (43) but our limited data support those of Pribula and Drago[158] with respect to a ligand exchange mechanism.

The ^{1}H n.m.r. spectra for the arene tricarbonyl metal-complexes (38) and (39) show upfield shifts for the methylene and aromatic ring protons compared to the non-complexed siloxane (8), and similarly, these effects were seen for identical groups in compounds (10) and (40). The aromatic

protons being closest to the metal centre, experience the greatest change in chemical shift on complexation, and for the Cr and Mo tricarbonyl compounds (38) and (39) respectively they are δ 1.76 and 2.68. This is a typical feature when group VI metals are involved, and it is well established that the shielding effects for the $M(CO)_3$ moiety are greatest for chromium, followed by tungsten and molybdenum.[159] Compounds (38) and (40) both contain the $Mo(CO)_3$ moiety and differ only in respect of the alkyl spacer chain length separating the silicon centre from the phenyl ring, but there is a significant difference between the chemical shifts of the aromatic protons of each metallated ligand which resonate at δ 5.42 and 4.72 respectively. This difference was not found for their respective ^{13}C aromatic carbon resonances which range between δ 91.55 and 96.04. Within unsymmetrically alkyl substituted arene complexes the chemical shifts of the individual ring protons are often different, and this has been attributed to differences in the π-electron density of the arene ring carbon atoms[160] which can also be influenced by other factors such as ring currents and magnetic anisotropy effects. This is a result of the metal carbonyl moiety being in a preferred conformation with respect to the ring, and consequently shielding influences on ring protons become unequal and are reflected in their chemical shift values.[161,162] The ^1H n.m.r. aromatic resonances for both compounds (39) and (40) appear as broad based sharp singlets with fine structure at the origin of the signal. This indicates that the $M(CO)_3$ group rotates relatively freely about the aromatic ring without any significant conformational preference at room temperature, and thus, on an n.m.r. time scale no permanent asymmetry results from complex formation. However, for compound (38) a closely grouped multiplet representing the aromatic protons was observed, and this signal would not be expected under the conditions described above. For this series of compounds a

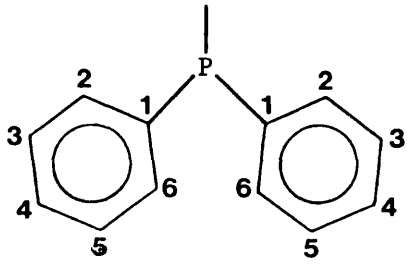
metal carbonyl resonance was only observed in the ^{13}C n.m.r. spectrum of (38) at δ 222.6, and this value correlates well with similar resonances recorded by Mann[163] for $M(CO)_3L$ M = Cr, Mo, or W; and L = an alkyl benzene where values range between δ 218.8 and 225.9 for the molybdenum complexed derivatives.

^{1}H and ^{13}C n.m.r. spectra were recorded for the metal halide phosphine complexes (31), (32) and (35), but not for (33), since this compound is paramagnetic and is not therefore expected to yield useful ^{1}H n.m.r. data. As mentioned previously, metallated siloxanes derived from compound (26) show extensive coupling between phosphorus and carbon in their ^{13}C n.m.r. spectra, and where possible coupling constants have been evaluated. For the palladium complex (31), the C_2 methylene group was observed as a well defined triplet with $J(^{31}P-^{13}C)$ = 13.42 Hz. The spectrum of the platinum analogue (32) was insufficiently well resolved in the C_1/C_2 region for coupling constants to be measured accurately. For compound (35), both methylene groups are coupled to the phosphorus nucleus and appear as well defined doublets with coupling constants of 7.0 and 70.3 Hz for C_1 and C_2 respectively. For compounds (31), (32) and (35) the relative ^{13}C shifts for the aromatic carbon atoms compared to those of the free ligand are listed and assigned[164,165] in Table 3.5.

The most significant ^{1}H and ^{13}C chemical shift changes on complexation were found for the iron carbonyl π-complexes (44) and (45). For example, in compound (44) the vinyl protons resonate at δ 1.83 and 2.62 compared to 6.25 in the original siloxane. In the ^{13}C n.m.r. spectrum of the original siloxane, the C_1 and C_2 atoms resonate at δ 137.5 and 132.0 respectively, while the signals of the same atoms in the π-complex (44) are shifted upfield to δ 41.85 and 40.36 respectively. Similar shifts

Table 3.5 ^{13}C n.m.r. data for selected metallated organosiloxanes

Compound	C_1	C_2/C_6	C_3/C_5	C_4
(26)	139.30(d, 13.7)	132.80(d, 18.3)	128.30(d, 3.7)	134.00(d, 17.1)
(31)	123.33(d, 45.2)	126.77(t, 6.11)	121.03(t, 9.77)	123.14
(32)		133.50(t, 4.88)	128.03(t, 4.88)	130.63
(35)	134.86	130.57(d, 9.77)	128.27(d, 10.28)	131.28(d, 2.44)



were observed between compounds (20) and (45) for those carbon atoms involved in complex formation. In the ^{13}C spectra, single resonances was observed for the $Fe(CO)_4$ moiety at δ 211.7 and 210.7 in (44) and (45) respectively, and these values agree closely with those of iron carbonyl π-complexes of simple silanes and siloxanes prepared by Rybinskaya et al.[96]

For compounds (36), (37) and (42), there were no significant changes in ^1H or ^{13}C n.m.r. chemical shifts compared to those found in their respective free ligands, with only small upfield shifts being noted. The $Mo(CO)_4$ moiety was located in the ^{13}C n.m.r. spectra of (36) and (42) at δ 211.2 and 205.7 respectively, with a very weak signal for the trans-isomer of (42) at δ 221.0. The assignment of metal carbonyl signals in cis- and trans-isomers of $Mo(CO)_4(L)_2$ has been made by a number of workers[166-168] with the latter isomer resonating at lower field in each of the cases referenced.

3.4 MISCELLANEOUS METAL COMPLEXATION REACTIONS

As stated in Section 2.2, the Friedal Crafts reaction between mesitylene and dichloromethylvinylsilane yielded a mixture of chlorosilane addition products, which on hydrolysis in the presence of chlorotrimethylsilane produced an analogous mixture of siloxanes which were not separable by fractional distillation. A sample of this mixture which contained $(Me_3SiO)_2SiMe(CH_2CH_2\text{-}2,4,6,Me_3C_6H_2)$ as the major component was reacted with $Mo(CO)_3(py)_3$ using a similar procedure to that used for the preparation of compound (38). Thin layer chromatography showed the crude product mixture to consist of the product complex and unreacted starting materials, which were separated by column chromatography as for (38). The product was isolated as a yellow oil in 63% yield, which although air-sensitive was of superior stability compared to the molybdenum tricarbonyl complexes (38) and (40). An infrared spectrum recorded for a neat sample showed two metal carbonyl bands at 1958s and 1878s cm^{-1} which clearly indicated the presence of the fac-$Mo(CO)_3$ moiety. ^1H and ^{13}C n.m.r. spectra were also recorded for this compound, and spectral data together with similar parameters tentatively assigned for the free ligand $(Me_3SiO)_2SiMe(CH_2CH_2\text{-}2,4,6,Me_3C_6H_2)$ are listed in Table 3.6. Figure 3.7 illustrates a ^{13}C OFR spectrum for the complexed siloxane.

On comparism of the ^1H and ^{13}C n.m.r. spectra for the free and complexed siloxane, the most significant upfield chemical shift changes were found for those atoms of the aromatic ring, and these observations follow from the n.m.r. spectral results found for compounds (38) - (40). The ^{13}C chemical shifts for the free and complexed ring are very similar to those found by Mann[163] for $Mo(CO)_3$(mesitylene) (δ $^{13}CH_3$, 21.2; ^{13}CH, 94.7;

^{13}CMe, 111.7). A single ^{13}C n.m.r. resonance for the $Mo(CO)_3$ moiety was observed at δ 229.5, which was found to be comparable in value to other molybdenum carbonyl complexed arenes.[163,169]

Table 3.6 ^{1}H and ^{13}C n.m.r. data for free and $Mo(CO)_3$ complexed $(Me_3SiO)_2SiMe(CH_2CH_2\text{-}2,4,6,Me_3C_6H_2)$

	Free ligand		$Mo(CO)_3$ complex	
Me_3Si	0.13(18H, s)	1.81	0.10(18H, s)	2.38
MeSi	0.13(3H, s)	-0.41	0.08(3H, s)	0.22
C_1/H_1	0.71(2H, m)	18.42	0.68(2H, m)	20.59
C_2/H_2	2.57(2H, m)	26.14	2.48(2H, m)	23.19
CMe	2.27(9H, m)	19.37, 22.41	2.24(9H, m)	19.56, 21.83
Aromatics	6.85(2H, m)	129.31, 135.49	5.24(2H, m)	95.94, 113.49

After synthesising and characterising $\left\{Me_3SiO\left[SiMe(CH_2CH_2PPh_2)O\right]_2SiMe_3\right\}PdCl_2$ (46), we used a similar procedure in an attempt to prepare a platinum metallated analogue. For two independent preparations using $PtCl_2(MeCN)_2$ and siloxyphosphine (27) in acetone and dichloromethane with refluxing for 16 and 3 hours respectively, white powders were isolated after purification by column chromatography as for (46). Infrared spectra for both samples were identical, with Pt-Cl stretching at 312 and 290 cm^{-1}. However, the carbon analyses for $\left\{Me_3SiO\left[SiMe(CH_2CH_2PPh_2)O\right]_2SiMe_3\right\}PtCl_2$ were consistently low, (Found: C, 37.43, 35.53; H. 5.11, 5.54; Cl, 7.40, 6.95. $C_{36}H_{52}Cl_2O_3P_2PtSi_4$ requires C, 44.40; H, 5.35; Cl, 7.30%), and we are unable to account for these findings.

The osmium cluster $H_2Os_3(CO)_{10}$, prepared by the reaction of hydrogen at atmospheric pressure on a hydrocarbon solution of $Os_3(CO)_{12}$,[170] readily undergoes addition reactions with donor ligands (L) to produce intermediates of the type $H_2Os_3(CO)_{10}L$ (L = CO, PMe_2Ph, PPh_3 or PhCN). The cluster $H_2Os_3(CO)_{10}PPh_3$, and other supported analogues on diphenylphosphine functionalised polystyrene and silica have been used as efficient catalysts for olefin isomerisation reactions.[171,172] By a similar procedure to that used by Freeman et al[172] we prepared $\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]H_2Os_3(CO)_{10}$ in 91% yield from the reaction of $H_2Os_3(CO)_{10}$ with compound (26) in hexane under a nitrogen atmosphere at ambient temperature. The product was purified by column chromatography using fluorosil (100-200), eluting initially with hexane to remove unreacted $H_2Os_3(CO)_{10}$, then benzene to elute the product. After removal of solvents in vacuo the product was isolated as an air stable yellow gum. The complex was identified by infrared spectroscopy with metal carbonyl absorptions at 2102m, 2063s, 2048s, 2021vs, 1978m and 1967m cm^{-1} in cyclohexane solution. These bands correspond closely to those of $H_2Os_3(CO)_{10}PPh_3$ at 2105m, 2066s, 2051s, 2025vs, 2017vs, 2004m, 1983m and 1971m cm^{-1} recorded under similar conditions,[171] and provide the basis for the formulation given.

3.5 SYNTHESES OF METAL-COMPLEXED ORGANOSILOXANES

The syntheses of transition-metal complexes used in the following preparations were by literature methods as listed in Appendix I. All chromatographic separations were on fluorosil (100-200 mesh) unless otherwise stated.

$\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]_2PdCl_2$ (31)

To $PdCl_2(PhCN)_2$ (0.20 g, 52 mmol) in anhydrous acetone (60 ml) was added

dropwise with rapid stirring compound (26) (0.452 g, 1.04 mmol). On addition the solution colour changed from deep red to yellow. After stirring at ambient temperature for 2h, the solvent and volatiles were removed under vacuum. The residual mixture was separated by column chromatography on fluorosil using hexane as eluant with collection of a yellow band. Removal of solvent followed by recrystallisation from hexane yielded the title compound as a yellow solid (0.48 g, 88%) m.p. 83°C (Found: C, 46.42; H, 7.06; P, 5.51. $C_{42}H_{70}Cl_2O_4P_2PdSi_6$ requires C, 48.23; H, 6.69; P,5.93%).

$\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]_2PtCl_2$ (32)

To $PtCl_2(MeCN)_2$ (0.12 g, 34.5 mmol) in acetone (35 ml) was added compound (26) (0.30 g, 68.9 mmol) dropwise with rapid stirring. After heating under reflux for 24h, solvent and volatiles were removed under vacuum. The reaction mixture was separated by column chromatography on fluorosil, eluting first with hexane and then ethyl acetate. The pure product was isolated as white crystals after recrystallisation from acetone/hexane (0.094 g, 24%) m.p. 108°C (Found: C, 45.40; H, 6.51; P, 5.29. $C_{42}H_{70}Cl_2O_4P_2PtSi_6$ requires C, 44.44; H, 6.17; P, 5.46%).

$\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]_2NiCl_2$ (33)

To $NiCl_2(MeCN)_2$ (0.05 g, 0.23 mmol) in dichloromethane (20 ml) was added (26) (0.205 g, 0.46 mmol) in dichloromethane (3 ml) dropwise with rapid agitation at ambient temperature. The solution was stirred overnight at this temperature whereupon a colour change from light green to cherry red occurred. The reaction mixture was reduced to low volume (ca 2 ml) in vacuo before purifying by column chromatography on fluorosil using hexane as eluant. The title compound was isolated as a purple solid after

removal of solvent in vacuo (0.19 g, 80%) m.p. 53°C (Found: C, 49.43; H, 7.21. $C_{42}H_{70}Cl_2NiO_4P_2Si_6$ requires C, 50.51; H, 7.01%).

$\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]_2Rh(CO)Cl$ (34)

To $\left[Rh(CO)_2Cl\right]_2$ (0.266 g, 68.6 mmol) in benzene (6 ml) was added dropwise with stirring at ambient temperature a solution of compound (26) (1.187 g, 2.73 mmol) dissolved in benzene (6 ml). The solution was heated under reflux until $\nu(C\equiv O)$ of $\left[Rh(CO)_2Cl\right]_2$ had disappeared ($\approx$5h). The solution was reduced to low volume (ca 2 ml) before separation by column chromatography on fluorosil eluting with acetone/petroleum-ether (40-60) (1:9 (v/v)) with collection of a dark yellow band. The product was isolated as a brown solid on evaporation of the solvent (0.78 g, 55%) m.p. 40°C.

$\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]_3RhCl$ (35)

To $\left[RhCl(C_2H_4)_2\right]_2$ (0.135 g, 34.7 mmol) dissolved in benzene (20 ml) was added a benzene (3 ml) solution of compound (26) (0.903 g, 2.08 mmol). The addition was made dropwise with stirring at ambient temperature. The mixture was stirred for a further 1.5h at this temperature before purifying by the procedure used for compound (34). The product was isolated as a red/brown gum (0.89 g, 86%).

$\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]_2Mo(CO)_4$ (36)

To $Mo(CO)_4(COD)$ (0.11 g, 34.6 mmol) in toluene (20 ml) was added compound (26) (0.295 g, 69.2 mmol). The mixture was heated under reflux for 3h before removal of solvent and volatiles under vacuum. The residual oil was purified by column chromatography using fluorosil, and eluting with hexane/ethyl acetate (2:1 v/v) with collection of a

yellow band. After removal of solvents in vacuo, the product (36) was isolated as a yellow oil (0.29 g, 63%).

$\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]Mo(CO)_3(bipy)$ (37)

To $Mo(CO)_4(bipy)$ (0.12 g, 33 mmol) in toluene (15 ml) was added a solution of (26) (0.287 g, 66 mmol) in toluene (3 ml). After boiling the mixture for 4h, the solution was cooled and the solvent and volatiles removed under vacuum leaving a purple solid. Purification was by column chromatography on fluorosil using first hexane to remove any unreacted phosphine (26), and then acetone which eluted a purple band. After removal of both solvents in vacuo, the product (37) was isolated as a purple solid (0.205 g, 73%) (Found: C, 52.90; H, 5.66; N, 3.52. $C_{34}H_{43}MoN_2O_5PSi_3$ requires C, 53.05; H, 5.59; N, 3.64%).

$\left[(Me_3SiO)_2SiMe(CH_2CH_2Ph)\right]Mo(CO)_3$ (38)

$BF_3.OEt_2$ (1.30 g, 9.2 mmol) was added dropwise with stirring to $Mo(CO)_3(py)_3$ (1.28 g, 3.07 mmol) and compound (8) (1.00 g, 3.07 mmol) in diethyl ether (50 ml). The mixture was stirred at ambient temperature for 1.5h before diluting with hexane (100 ml). The mixture was washed with distilled water (3 x 100 ml), and the organic layer separated, filtered, and dried over anhydrous Na_2SO_4. The solvents and volatiles were removed in vacuo leaving a yellow oil. The oil was purified by column chromatography on fluorosil, eluting with hexane then benzene with collection of a yellow band. After removal of the solvents in vacuo. the title compound (38) was isolated as a bright yellow oil (0.93 g, 60%), and identified from spectroscopic analysis.

$\left[(Me_3SiO)_2SiMe(CH_2CH_2Ph)\right]Cr(CO)_3$ (39)

Compound (8) (1.50 g, 4.57 mmol) and $Cr(CO)_6$ (1.00 g, 4.57 mmol) in glyme (35 ml) were heated carefully to 70 °C for 3h. On warming to 70 °C the solution gradually became yellow, and when there was no further increase in colour intensity the solution was cooled and filtered to remove insoluble chromium salts. The filtrate was reduced to low volume (ca 3 ml), and the product was isolated as a yellow oil by column chromatography as for compound (38), (0.22 g, 10%).

$\left[(Me_3SiO)_2SiMe(CH_2CH_2CH_2Ph)\right]Mo(CO)_3$ (40)

This compound was prepared by a similar procedure to that used for (38), starting from (10) (0.65 g, 1.91 mmol), $Mo(CO)_3(py)_3$ (0.796 g, 1.91 mmol) and $BF_3.OEt_2$ (0.815 g, 5.73 mmol). The product was isolated as an air-sensitive, yellow oil (0.49 g, 50%) and identified by infrared and nuclear magnetic resonance spectra.

$\left[(Me_3SiO)_2SiMe(CH_2CH_2CH_2C_5H_4N)\right]Rh(CO)_2Cl$ (41)

To $\left[Rh(CO)_2Cl\right]_2$ (0.133 g, 0.34 mmol) in benzene (12 ml) was added dropwise with stirring compound (25) (0.233 g, 0.68 mmol) in benzene (3 ml). The colour of the solution changed from lemon yellow to orange-brown on addition of the siloxane. After stirring at ambient temperature for 2h the solvent and volatiles were removed in vacuo. The reaction mixture was separated by column chromatography on fluorosil, eluting with hexane then ethyl acetate with collection of a yellow band. Following the removal of solvents in vacuo the product was isolated as an orange-brown oil (0.17 g, 46%), and identified by spectroscopic analysis.

$\left[(Me_3SiO)_2SiMe(CH_2CH_2CH_2C_4H_5N)\right]_2Mo(CO)_4$ (42)

This compound was synthesised by a similar procedure to that used for (36), from (25) (0.35 g, 1.02 mmol) and $Mo(CO)_4(COD)$ (0.161 g, 0.51 mmol), and was isolated as an air-sensitive yellow oil (0.29 g, 63%), and identified by spectroscopic analysis.

$\left[(Me_3SiO)_2SiMe(CH_2CH_2CH_2CN)\right]Rh(CO)_2Cl$ (43)

To $\left[Rh(CO)_2Cl\right]_2$ (0.152 g, 0.39 mmol) in benzene (20 ml) was added dropwise with stirring compound (12) (0.226 g, 0.78 mmol) dissolved in benzene (3 ml). The mixture was heated under gentle reflux for 3h, cooled, and the solvents and volatiles removed in vacuo. The orange oil isolated appeared analytically pure from thin layer chromatography and spectroscopic analysis which showed no evidence for unreacted starting materials, (0.36 g, 95%).

$\left[(Me_3SiO)_2SiMe(CH{=}CH_2)\right]Fe(CO)_4$ (44)

Compound (17) (1.00 g, 4.03 mmol) and $Fe_2(CO)_9$ (1.46 g, 4.03 mmol) in hexane (40 ml) were stirred for 14h at ambient temperature. During reaction the solution turned emerald green in colour. Unreacted $Fe_2(CO)_9$ was filtered off and the green filtrate and volatiles were evaporated in vacuo. The residue was separated by column chromatography on silica eluting with hexane. A yellow band was collected, and following the removal of solvent in vacuo the product (44) was isolated as an air-sensitive yellow oil (0.48 g, 29%) (Found: C, 38.28; H, 6.21. $C_{13}H_{24}FeO_6Si_3$ requires C, 37.50; H, 5.77%).

$\left[(Me_3SiO)_2SiMe(CH_2CH{=}CH_2)\right]Fe(CO)_4$ (45)

This compound was isolated as an air-sensitive yellow oil (0.25 g, 30%) on reaction of compound (20) (0.50 g, 1.91 mmol) and $Fe_2(CO)_9$ (0.694 g, 1.91 mmol) in hexane (35 ml) as above. Identification of this compound was by spectroscopic analysis.

$\left\{Me_3SiO\left[SiMe(CH_2CH_2PPh_2)O\right]_2SiMe_3\right\}PdCl_2$ (46)

This complex was prepared by a similar procedure to that used for compound (31), from (27) (0.221 g, 0.31 mmol) and $PdCl_2(PhCN)_2$ (0.12 g, 0.31 mmol) in acetone (25 ml), and was isolated as a yellow oil following column chromatography on fluorosil using hexane then acetone as eluants (0.30 g, 73%) (Found: C, 48.70; H, 5.47; Cl, 8.04. $C_{36}H_{52}Cl_2O_3P_2PdSi_4$ requires C, 48.90; H, 5.89; Cl, 8.04%).

Figure 3.1 ^{13}C n.m.r. spectrum of $\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]_2PdCl_2$ (31)

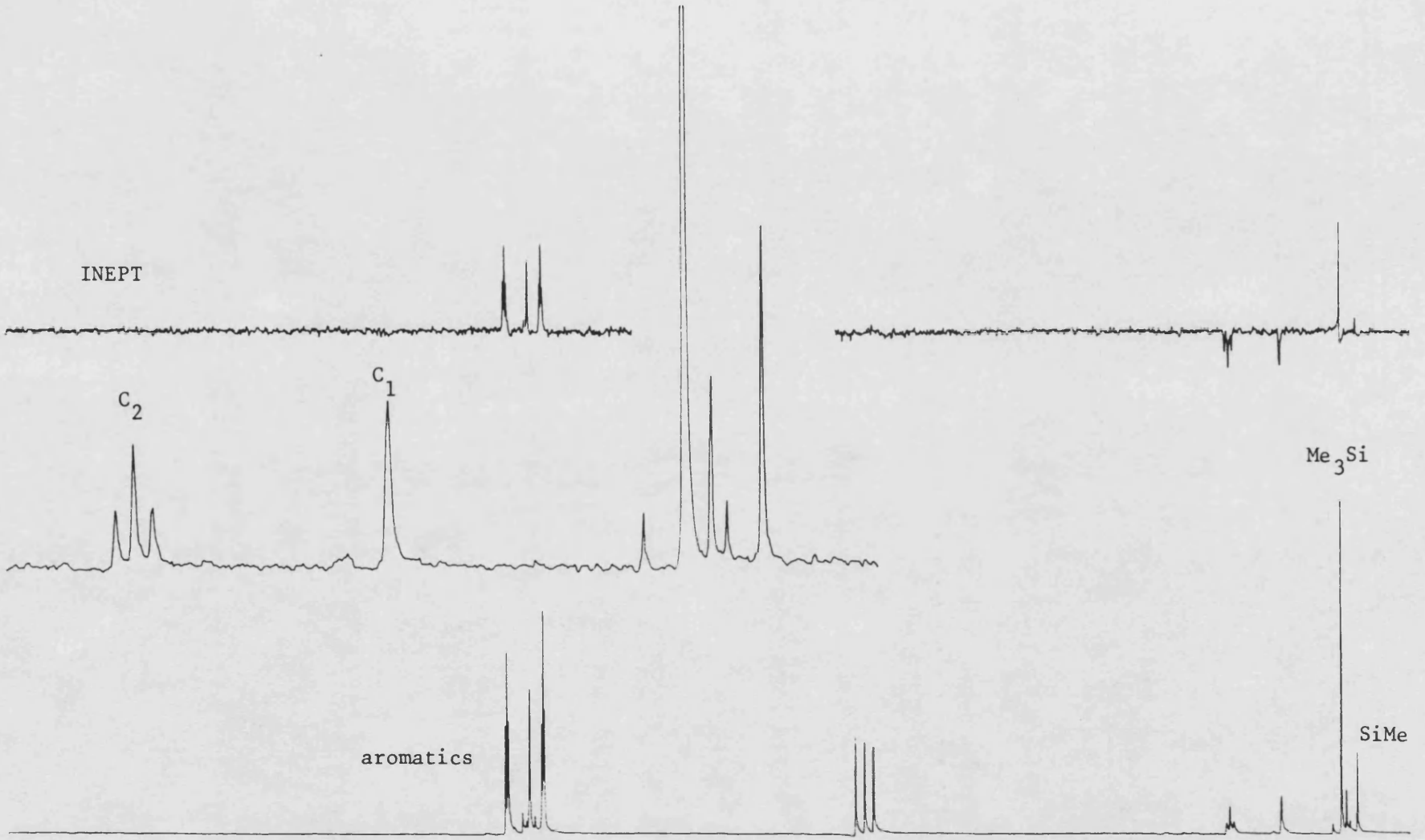


Figure 3.2 ^{13}C n.m.r. spectrum of $\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]_2Rh(CO)Cl$ (34)

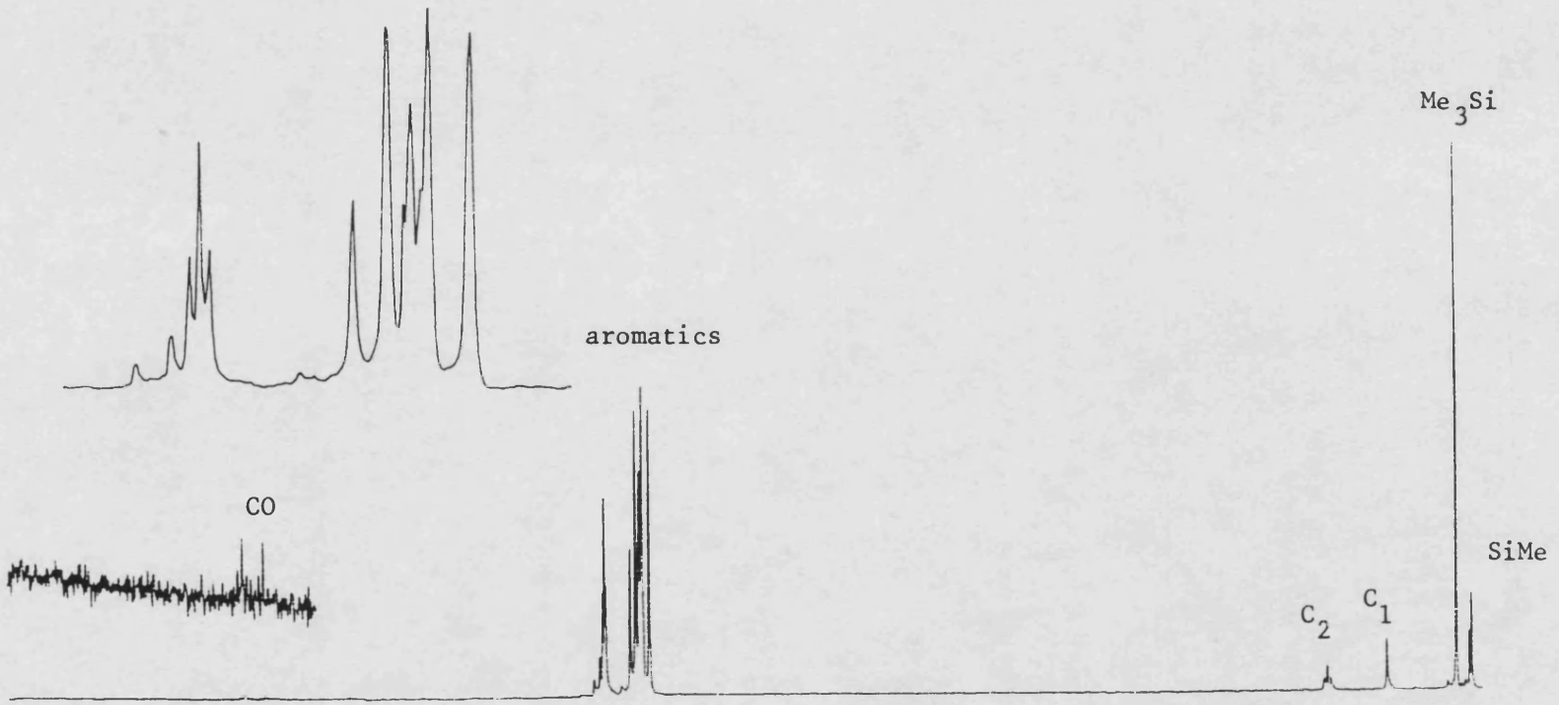


Figure 3.3 ^{13}C n.m.r. spectrum of $\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]_3RhCl$ (35)

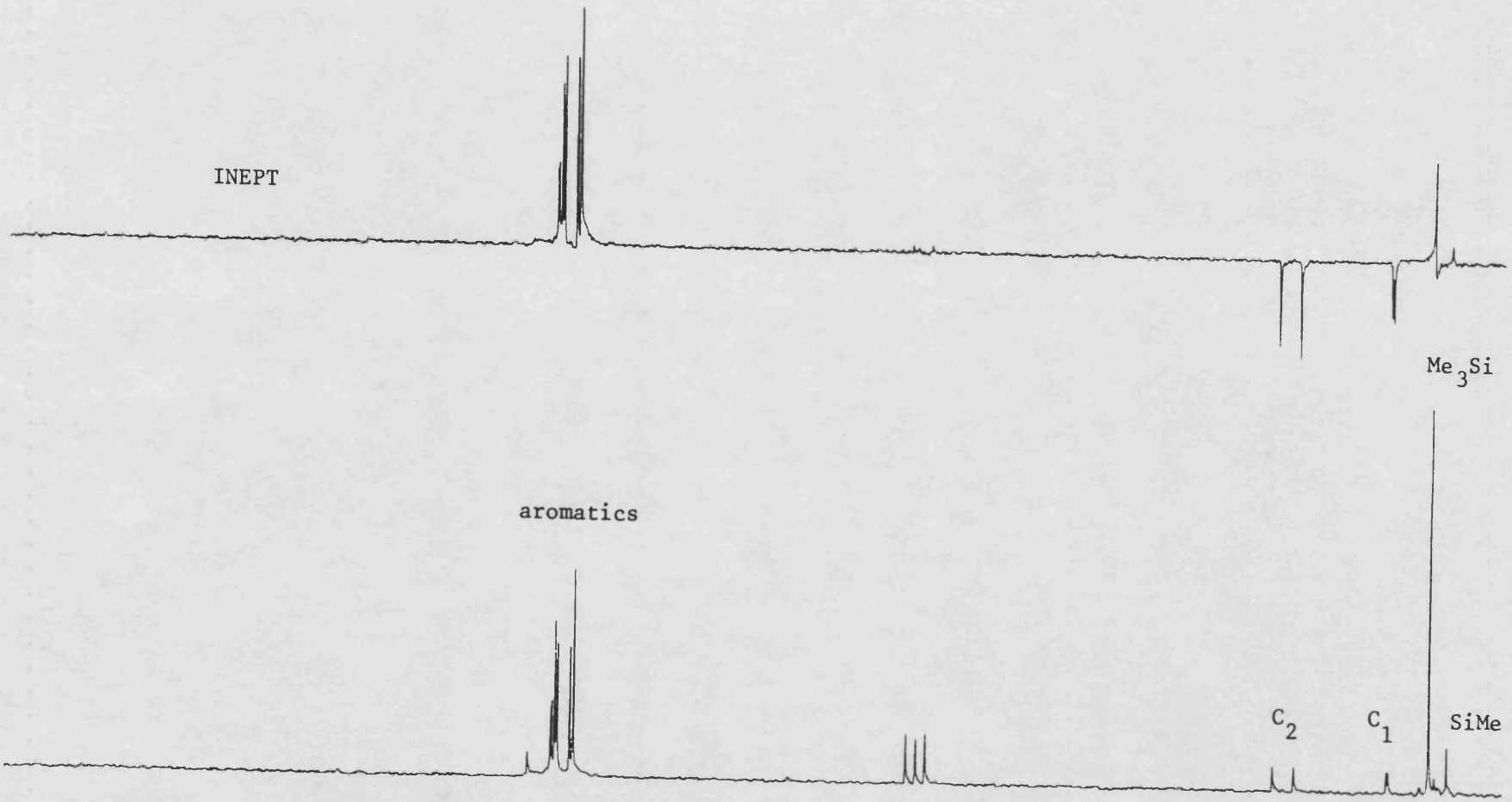


Figure 3.4 ^{13}C n.m.r. spectrum of $\left[(Me_3SiO)_2SiMe(CH_2CH_2CH_2C_5H_4N)\right]Rh(CO)_2Cl$ (41)

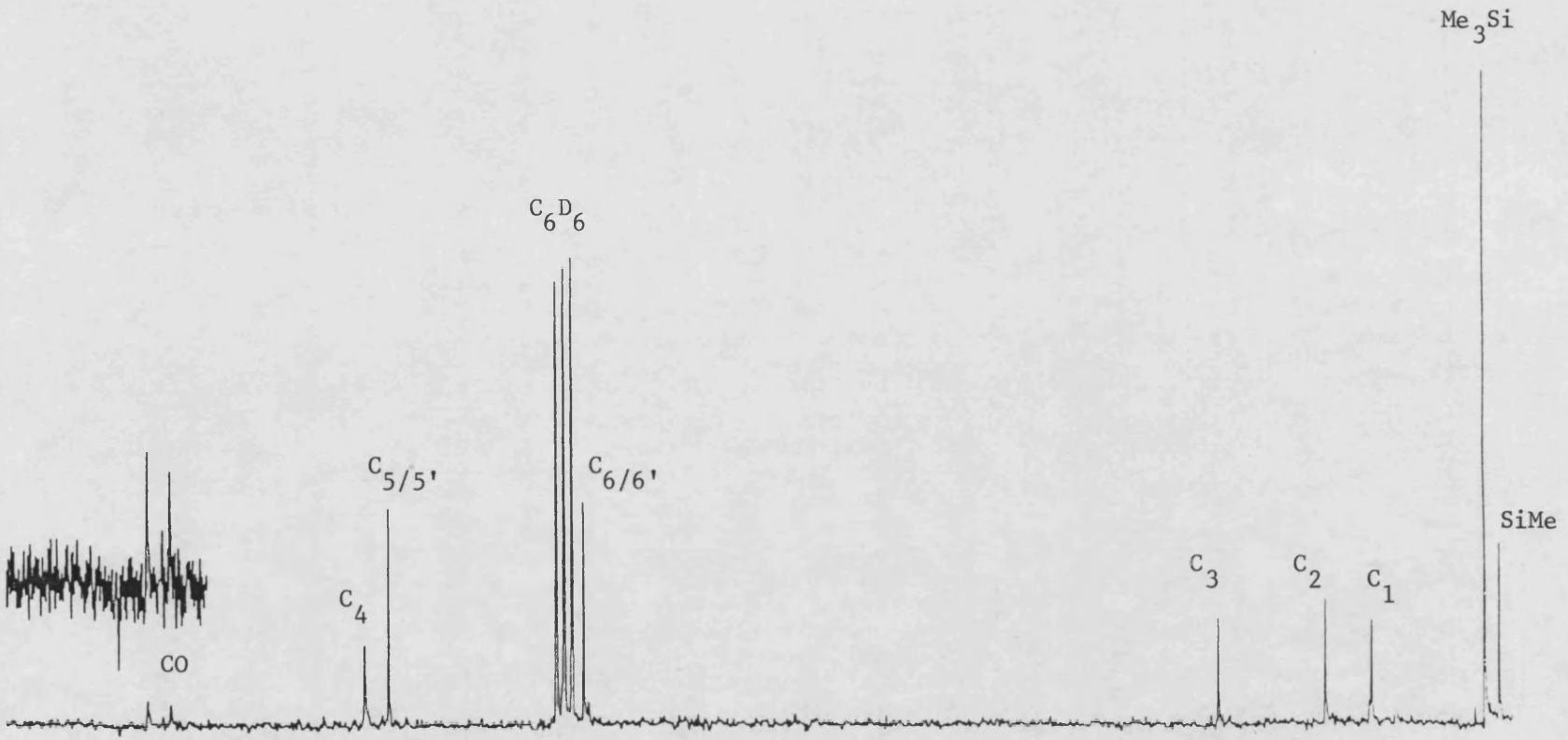


Figure 3.5 ^{13}C n.m.r. spectrum of $\left[(Me_3SiO)_2SiMe(CH_2CH_2CH_2CN)\right]Rh(CO)_2Cl$ (43)

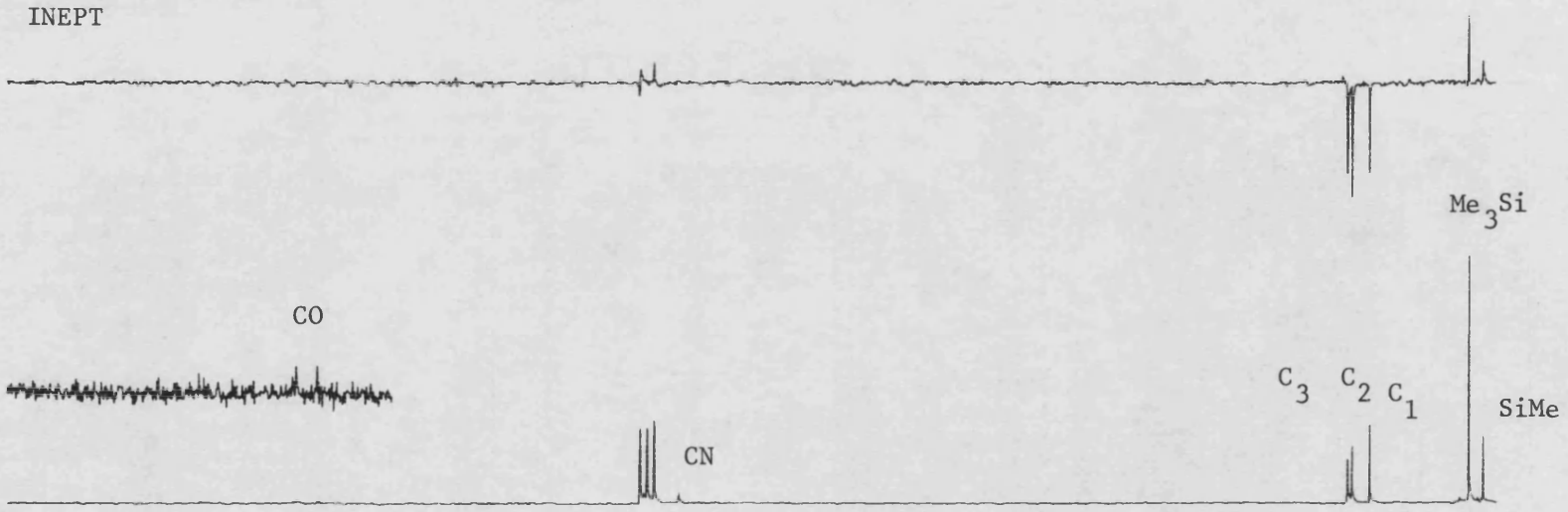


Figure 3.6 ^{13}C n.m.r. spectrum of $\left[(Me_3SiO)_2SiMe(CH_2CH{=}CH_2)\right]Fe(CO)_4$ (45)

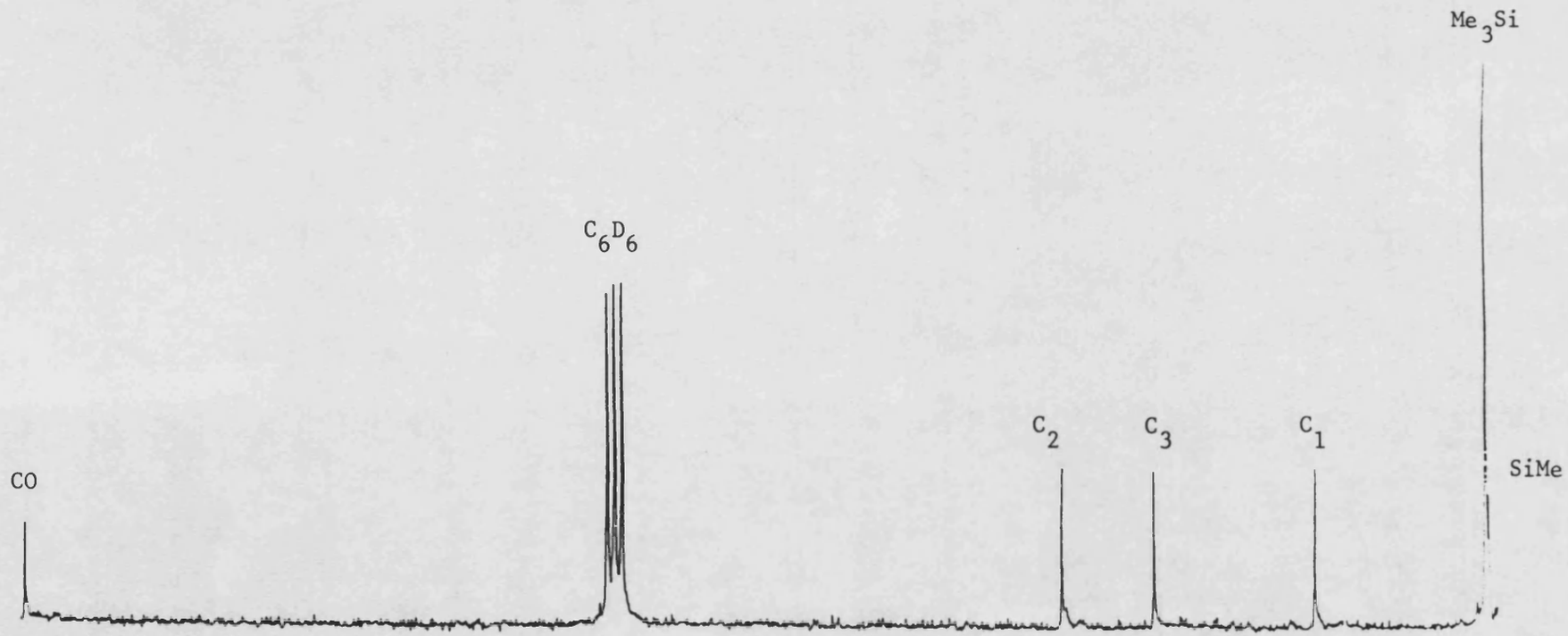
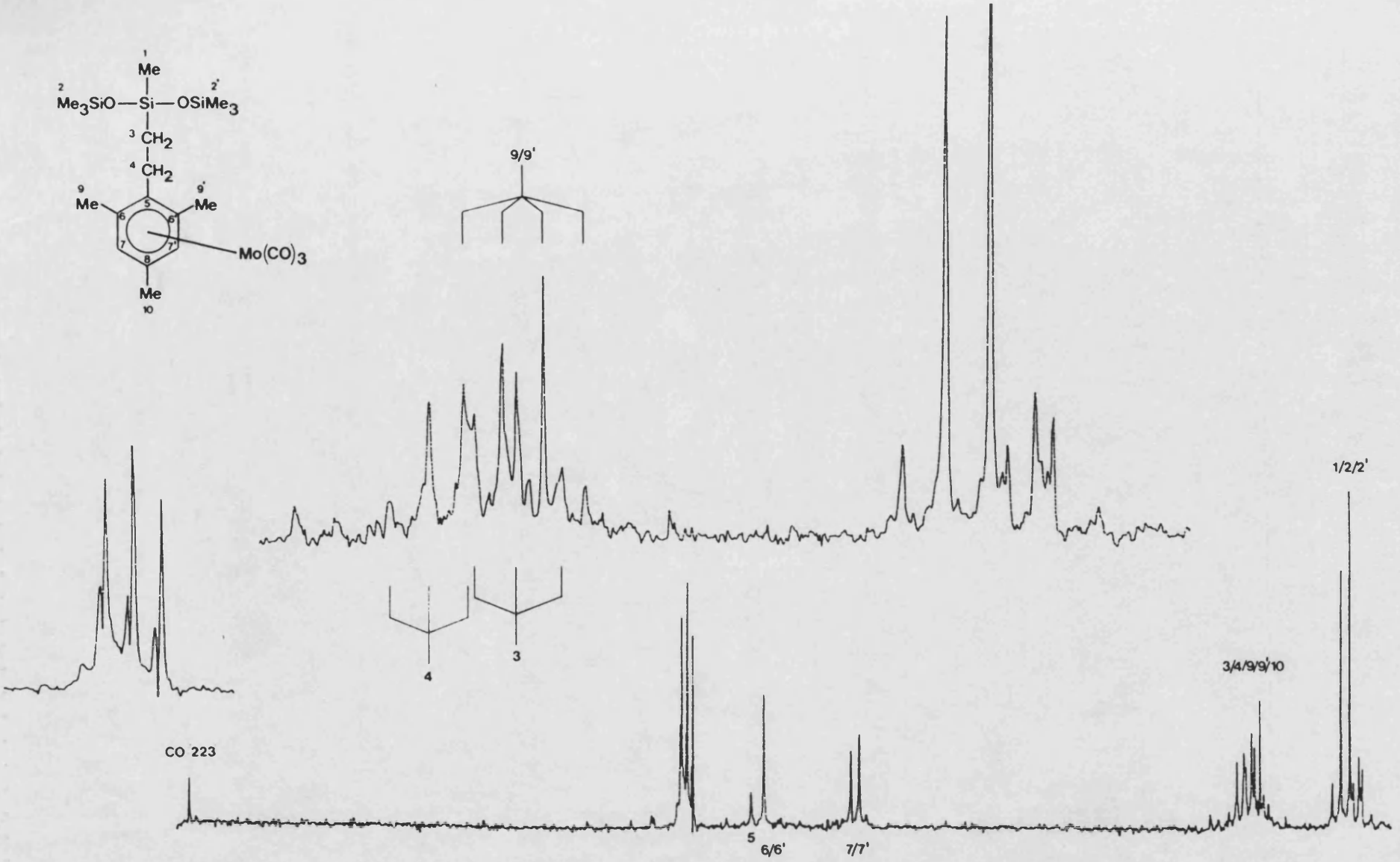


Figure 3.7 ^{13}C n.m.r. OFR spectrum of $\left[(Me_3SiO)_2SiMe(CH_2CH_2\text{-}2,4,6,Me_3C_6H_2)\right]Mo(CO)_3$



CHAPTER FOUR

FUNCTIONALISED POLYSILOXANES AND SUPPORTED METAL CATALYSTS

4.1 INTRODUCTION

The third section of these studies has focused initially on the preparation and characterisation of cyclic and linear polysiloxanes which have been functionalised with metal-anchoring groups, or with groups capable of being chemically modified into pendant ligands, which may support transition-metal catalysts. Many of the linear polysiloxanes have been derived from their model organosiloxane analogues and derivatives bearing the nitrile, arene, hydrido, vinyl, bromo and phosphine moieties were successfully synthesised, whereas in the case of the cyclopolysiloxanes low molecular weight polymers incorporating the latter three functional groups only were prepared.

The next phase involved interaction of selected polymers with transition-metal species, and in the case of the arene and phosphine functionalised polysiloxanes, metal complexed derivatives which were analogous to their model metallated organosiloxanes were synthesised and characterised.

4.2 SYNTHETIC METHODS

4.2.1 LIGAND FUNCTIONALISED POLYSILOXANES

The methods employed for the preparation of functionalised cyclic and linear polysiloxanes were modelled, where possible, on the procedures used for the analogous tri-, tetra- and pentasiloxanes listed in Chapter 2.

The cyclic vinylsiloxane $\left[SiMe(CH{=}CH_2)O\right]_4$ (47) was obtained from Dow Corning as a commercial sample, and was separated from lower and higher boiling vinylsiloxanes by fractional distillation. This compound (presumably consisting of a mixture of isomers) was isolated as a colourless air stable oil and has proved to be a useful starting material for the synthesis of (48), (49) and linear polyvinylsiloxanes.

$$\left[SiMe(CHBrCH_2Br)O\right]_4 \qquad (48)$$

$$\left[SiMe(CH_2CH_2PPh_2)O\right]_4 \qquad (49)$$

The dibromo functionalised cyclosiloxane (48) was prepared by addition of bromine across the vinyl group of compound (47) in carbon tetrachloride (equation (60)).

$$\left[SiMe(CH{=}CH_2)O\right]_4 \xrightarrow{Br_2} \left[SiMe(CHBrCH_2Br)O\right]_4 \qquad (60)$$

This reaction proceeded very smoothly at ambient temperature affording complete saturation of the carbon-carbon double bond in (47), as demonstrated by both infrared and ^1H n.m.r. spectroscopies. The excess unreacted bromine was removed by pumping in vacuo leaving (48) as a light brown viscous oil.

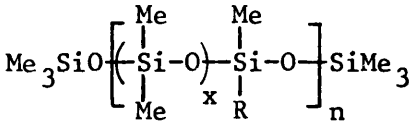
By using a very similar procedure to that employed for the preparation of compounds (26)-(29), the phosphine functionalised cyclosiloxane (49) was synthesised in high yield by reacting stoichiometric quantities of (47) and diphenylphosphine, (equation (61))

$$\left[SiMe(CH{=}CH_2)O\right]_4 \xrightarrow{HPPh_2} \left[SiMe(CH_2CH_2PPh_2)O\right]_4 \qquad (61)$$

This particular siloxyphosphine was isolated as an air-sensitive colourless glass which transformed into a mobile oil on warming, and was the only example of a solid polymer being formed in our studies.

The approach adopted for studies on linear polysiloxanes involved the preparation of polymers whose functional group spacing could be determined, and whose degree of metallation after reaction with

transition-metal complexes could be estimated by chromatographic and spectroscopic techniques. From these results average formulae for all materials could then be assigned. The linear polysiloxanes prepared were all true polymers and can be represented by the following formulae.



Compound	R	x
(50)	$CH{=}CH_2$	8
(51)	$(CH_2)_2Br$	8
(52)	$(CH_2)_2PPh_2$	8
(53)	$(CH_2)_2Ph$	6
(54)	$(CH_2)_3CN$	5
(55)	H	12

The two polymerisation procedures used have both involved equilibriating mixtures of siloxanes. In each case the mixture consisted of a siloxane or silanol derivative containing the appropriate functionality together with octamethylcyclotetrasiloxane $(SiMe_2O)_4$, and hexamethyldisiloxane $(SiMe_3)_2O$. In the presence of an acid, $(SiMe_2O)_4$ is readily cleaved at a siloxane bond to produce a linear octamethyltetrasiloxane unit, which can take part in a series of addition reactions with other siloxanes to produce high molecular weight polymers. In the presence

of $(SiMe_3)_2O$ these polysiloxanes become end-blocked by trimethylsilyl groups, and the concentration of this disiloxane determines the chain length of each polymer since the rate of acid catalysed cleavage of Me_3SiO- compared to Me_2SiO- is low.

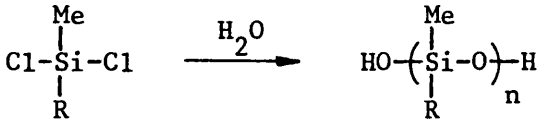
The vinyl polymer (50) was one of many such polysiloxanes ((50a) - (50e)) prepared by the acid catalysed equilibriation of $\left[SiMe(CH{=}CH_2)O\right]_4$, $(SiMe_2O)_4$ and $(SiMe_3)_2O$, with the relative amounts of each siloxane being varied to produce, on average, a vinyl group every six to eight silanone groups and a mean average molecular weight approaching 21000.

$$\left[SiMe(CH{=}CH_2)O\right]_4 + (SiMe_2O)_4 \xrightarrow[(SiMe_3)_2O]{TFMSA} Me_3SiO\left[\begin{array}{c} Me \\ (Si\text{-}O)_8 \\ Me \end{array}\right]\left[\begin{array}{c} Me \\ Si\text{-}O \\ CH{=}CH_2 \end{array}\right]_n SiMe_3 \qquad (62)$$

The polysiloxane (50), having 19.7 mol % of vinyl groups, was the only polymer to be fully characterised and used in a further series of reactions. The polymerisation procedure involved mixing the siloxanes (47), $(SiMe_2O)_4$ and $(SiMe_3)_2O$ at ambient temperature under a nitrogen atmosphere. After addition of TFMSA (trifluoromethylsulphonic acid) as catalyst, the mixture was heated to a selected elevated temperature. The polymerisation was assumed to be complete when the siloxane components had reached a dynamic equilibrium which was indicated by the solution having a constant viscosity, after which neutralisation of the catalyst with dimethylformamide (DMF) and subsequently removing by filtration yielded a mixture of linear polysiloxanes and low molecular weight cyclic dimethylsiloxanes. The linear polysiloxanes were freed from cyclic siloxanes by either distillation under reduced pressure or by preparative

gel permeation chromatography. For polymers which were purified by preparative GPC, the procedure was based on finding an optimum sample concentration which produced well separated elution volume curves for the components present without causing overloading of the column material. The solution flows within the equipment were designed and regulated so that sample components could be collected as their elution curves were observed on the recorder.

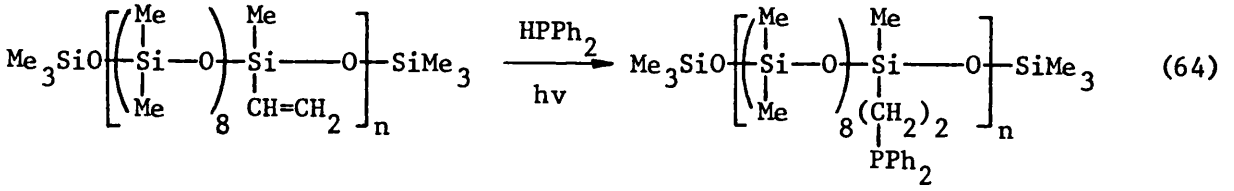
The functionalised polysiloxanes (53) - (55) inclusive were all prepared using similar polymerisation techniques. The functional group in each polymer was derived from the appropriate dichlorosilane, and the use of such compounds in polymerisation processes prevented the formation of cross-linked polymers. The initial step in each case was careful hydrolysis of the chlorosilane at low temperature with a stoichiometric amount of water to produce a mixture of silanol species, i.e.



(63)

During this hydrolysis reaction a stream of nitrogen was bubbled through the solution to displace hydrogen chloride gas to minimise hydrochloric acid formation and hence reduce siloxane bond cleavage. The silanol species was mixed <u>in situ</u> with $(SiMe_2O)_4$ and $(SiMe_3)_2O$, and equilibriated at a constant elevated temperature in the presence of TFMSA as catalyst. After equilibriation was complete and the acid catalyst had been neutralised with DMF, the polysiloxane mixture was diluted, dried and filtered. Finally, all of the low molecular weight by-products were removed by procedures described above leaving a mixture of functionalised linear polysiloxanes.

After synthesising a range of different molecular weight polyvinylsiloxanes the next phase was to functionalise a polymer which could serve as a support matrix for anchoring transition-metal complexes. Polysiloxane (50) conformed most closely to our requirements in terms of mean average molecular weight and vinyl group spacing within the polymer, and was selected for further functionalisation. The diphenylphosphine group has been widely used in catalytic supports, and in view of the ease with which $HPPh_2$ adds to vinylsiloxanes under photochemical conditions, we used this proven method to prepare a diphenylphosphine functionalised linear polysiloxane (52). After having accurately characterised the vinyl polymer precursor (50), the stoichiometric quantity of $HPPh_2$ necessary for complete saturation of all the vinyl groups present could be calculated accordingly.



(64)

The siloxyphosphine polymer was isolated as an air-sensitive viscous white oil which was used without purification.

The bromo functionalised polysiloxane (51) was synthesised in high yield by the organic peroxide catalysed anti-Markownikoff addition of hydrogen bromide across the vinyl groups in (50) using a similar procedure to that employed for the preparation of compound (24). The brominated polymer was isolated as a colourless air-sensitive oil after pumping <u>in vacuo</u> to remove any residual hydrogen bromide.

4.2.2 METAL COMPLEXED POLYSILOXANES

In view of the excellent ligating properties of the siloxyphosphine (26) towards group VIII metals, further studies on the metallation reactions of both cyclic and linear polysiloxanes were limited (with one exception) to those functionalised with the diphenylphosphine group. The exception involved the linear arene polysiloxane (53).

The synthetic methods which were used to prepare both metal complexed cyclic and linear polysiloxanes were based on procedures developed for the corresponding metallated trisiloxanes described in Chapter 3. The three metallated cyclic siloxanes prepared from (49) are listed below.

$$\left[SiMe(CH_2CH_2PPh_2)O\right]_4Pd_2Cl_4 \qquad (56)$$

$$\left[SiMe(CH_2CH_2PPh_2)O\right]_4Pt_2Cl_4 \qquad (57)$$

$$\left[SiMe(CH_2CH_2PPh_2)O\right]_4Rh_2(CO)_2Cl_2 \qquad (58)$$

Compounds (56) and (57) were synthesised in high yields by the displacement of methyl cyanide from $MCl_2(MeCN)_2$ (M = Pd or Pt) in dichloromethane by (49). The complex $PdCl_2(MeCN)_2$ was used in preference to its phenyl cyanide analogue because of the greater volatility of methyl cyanide, which could be readily removed by pumping in vacuo. In order to prepare compound (56) the reaction was carried out at ambient temperature over a two hour period before removal of the solvent in vacuo. The residual solid was recrystallised from dichloromethane/hexane to give the pure product. A similar procedure was used for the platinum analogue (57), although a longer reaction time was necessary for complete replacement of the ligated nitrile. Compound (58) was prepared by heating (49) with

$\left[Rh(CO)_2Cl\right]_2$ in refluxing benzene, with the reaction being monitored by infrared measurements in the carbonyl region. On disappearance of CO bands associated with $\left[Rh(CO)_2Cl\right]_2$, the reaction was terminated and the metallated product isolated as an orange/brown solid after evaporation and purification by recrystallising from dichloromethane/ hexane.

The solubilities of compounds (56), (57) and (58) were qualitatively tested in a range of organic solvents which included dichloromethane and acetone, and it was found that all three compounds had relatively low solubilities, even on warming, when compared to their respective metallated trisiloxane counterparts.

A series of similar metal complexation reactions using the linear phosphine functionalised polysiloxanes (52) and (53) were carried out, and the supported catalysts prepared are listed below.

$$\left\{Me_3SiO\left[(SiMe_2O)_8SiMe(CH_2CH_2PPh_2)O\right]_nSiMe_3\right\}_2PdCl_2 \quad (59)$$

$$\left\{Me_3SiO\left[(SiMe_2O)_8SiMe(CH_2CH_2PPh_2)O\right]_nSiMe_3\right\}_2PtCl_2 \quad (60)$$

$$\left\{Me_3SiO\left[(SiMe_2O)_8SiMe(CH_2CH_2PPh_2)O\right]_nSiMe_3\right\}_2Rh(CO)Cl \quad (61)$$

$$\left\{Me_3SiO\left[(SiMe_2O)_8SiMe(CH_2CH_2PPh_2)O\right]_nSiMe_3\right\}_3RhCl \quad (62)$$

$$\left\{Me_3SiO\left[(SiMe_2O)_6SiMe(CH_2CH_2Ph)O\right]_nSiMe_3\right\}Mo(CO)_3 \quad (63)$$

$$\left\{Me_3SiO\left[(SiMe_2O)_8SiMe(CH_2CH_2PPh_2)O\right]_nSiMe_3\right\}H_2Os_3(CO)_{10} \quad (64)$$

The polysiloxane (52) was complexed with $MCl_2(MeCN)_2$ (M = Pd and Pt) and $\left[Rh(CO)_2Cl\right]_2$ using similar procedures to those outlined above. The supported palladium (59) and platinum (60) catalysts were isolated as golden and yellow gums respectively, whereas the rhodium carbonyl catalyst (61) was recovered as a golden brown solid. Compound (62), which is analogous to Wilkinson's catalyst, was prepared by reacting (52) with Cramer's complex $\left[RhCl(C_2H_4)_2\right]_2$ in benzene to yield the product as a fibrous brown solid. Polymeric siloxyphosphine rhodium(I) complexes have been prepared previously by the hydrolysis of preformed rhodium complexes,[89] but these insoluble systems containing the metal moieties Rh(CO)Cl and RhCl were both ill-defined and non-reproducible.

The decomposition temperatures of catalysts (59) - (62) were measured by heating samples in air using a conventional melting point apparatus, and the ranges were found to be 180 - 185, 305 - 315, 285 - 295, and 310 - 330 ^{o}C respectively. These values refer to the temperatures at which the samples started blackening, and at this point the metallic moieties were assumed to be decomposing.

As a result of the limited solubility found for compounds (56) - (58) in organic solvents, we anticipated that the linear polymeric analogues would exhibit similar properties. To confirm this assumption, the reaction mixture was divided into two equal volumes and one half was reduced to dryness *in vacuo* to yield the supported catalyst, while the second portion was treated with $(SiMe_2O)_4$ to produce a liquid phase catalyst. The amount of $(SiMe_2O)_4$ added was determined by the mass of supported catalyst present in the solution, in order that either a 25 or a 50% w/w solution was formed. On removal of the more volatile organic solvent *in vacuo*, viscous gums were recovered which showed good solubility in polar organic solvents compared to their non-SLPC

analogues.

The molybdenum complex $Mo(CO)_3(py)_3$ was reacted with the arene functionalised polysiloxane (53) in the presence of boron trifluoride etherate to yield a supported catalyst (63) bearing $Mo(CO)_3$ moieties. The synthetic procedure used was similar to that employed for the preparation of (38), except that no purification steps could be employed owing to the inherent instability of this type of metallated compound. The catalyst was isolated as a yellow gum which on standing under nitrogen darkened as decomposition occurred. This process was accompanied by diminishing carbonyl bands in the infrared spectra taken over a three hour period after isolation of the supported catalyst.

By a similar procedure to that used for the preparation of $\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]H_2Os_3(CO)_{10}$ a polysiloxane supported analogue (64) was synthesised in high yield by reacting $H_2Os_3(CO)_{10}$ with the polysiloxyphosphine (52) in hexane at ambient temperature. By using a functionalised polymer in which the phosphine moieties are well separated and can be considered 'dilute', the probability of only single bond formation between one phosphorus and one osmium atom are high compared to the equivalent metallation reaction using siloxyphosphine (26), where multiple substitution of carbonyl groups is possible in view of the greater effective mobility of the donor ligands in solution.

4.3 CHARACTERISATION OF LIGAND FUNCTIONALISED AND METAL COMPLEXED POLYSILOXANES

4.3.1 GEL PERMEATION CHROMATOGRAPHY

Gel permeation chromatography has been used in two ways to study functionalised polysiloxanes. Firstly, as an analytical tool to determine

the number of major components in a polymer sample and to evaluate their mean molecular weights, and secondly, on a preparative basis to isolate and purify one or more components from the mixture.

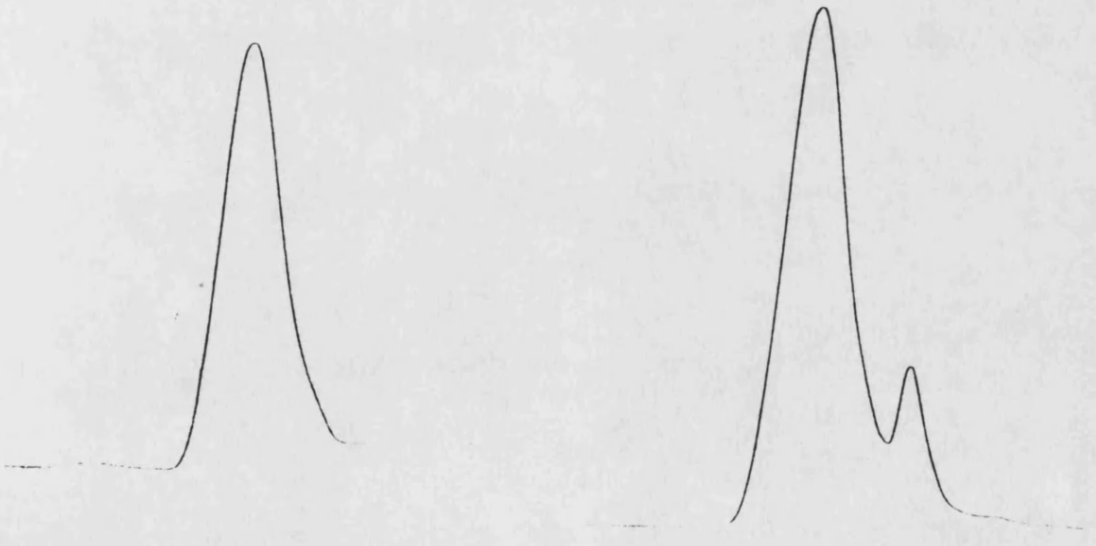
In all cases, GPC studies were made on toluene solutions of the polymers and molecular weight determinations were referenced to polystyrene standards analysed under the same physical conditions.

With the exception of the phosphine functionalised polymer (52), which was found to absorb irreversibly onto the column packing material, mean average molecular weights were found for the vinyl-, bromo-, nitrile-, phenyl- and hydrido- polysiloxanes, and a summary of typical results are listed in Table 4.1. For all of the preparative procedures involving equilibration processes, cyclic dimethylsiloxanes were present in varying amounts after cessation of polymerisation, and were readily identified from the GPC trace. Two such volume curves are illustrated below for polysiloxane (50) as, (a) a pure polymer, and (b) a sample prior to purification. The amount of cyclic dimethylsiloxanes present in a sample could not be calculated directly from the GPC trace since the method of detection was based on the refractive indices of the siloxanes present and not their individual weights as a proportion of the total sample weight. Generally, the molecular weights were found to be reproducible for identical samples, and minor inaccuracies were attributed to the physical measurements taken from the GPC traces. However, as an analytical tool GPC proved invaluable in this study.

Table 4.1 Mean average molecular weight data for functionalised polysiloxanes

Polysiloxane	M_w	Mol % functionality
(50)	21000	19.7
(51)	23500	19.7
(53)	14500	13.6
(54)	41700	16.6
(55)	17000	14.2

GPC volume curves for polysiloxane (50)



(a) (b)

4.3.2 INFRARED SPECTROSCOPY

Infrared spectra have been recorded for compounds (47) - (64), and a summary of significant absorption data for selected functionalised cyclic and polysiloxanes, together with those for a number of supported catalysts are listed in Table 4.2.

Table 4.2 Infrared absorption data for selected functionalised and supported metal catalysts

Compound	Infrared absorption frequency (cm^{-1})
(47)	3060m, 3022w, 2964m, 1601m, 1418m, 1264s, 1083s, 1028s, 968m, 832m,806s, 757s, 688m, 623m
(48)	2960w, 2942w, 1438w, 1418w, 1402sh, 1260s, 1222m, 1206m, 1100vs, 1025s, 885w, 870w, 785vs, 764s
(49)	3075s, 3055s, 3020m, 2960s, 2932s, 2900s, 1957w, 1888w, 1815w, 1586m, 1572w, 1480s, 1436vs, 1408s, 1431w, 1404m, 1260vs, 1192s, 1150vs, 1060vs, 792vs, 733vs, 715vs, 686vs
(50)	3060w, 2960vs, 2922m, 1600m, 1447w, 1412s, 1262vs, 1065vs, 960s, 818vs, 757s, 692s, 668s
(51)	2964s, 2904m, 1442w, 1417m, 1260vs, 1163s, 1060vs, 862s, 797vs, 700m, 662m
(52)	3075w, 3058w, 2960s, 2905m, 1586w, 1480w, 1436m, 1410m, 1260vs, 1152s, 1050vs, 860s, 797vs, 736s, 692s, 658m
(53)	3090w, 3072w, 3032m, 2968s, 2915m, 1602m, 1495m, 1456m, 1415m, 1260vs, 1180m, 1065vs, 868sh, 793vs, 760sh, 666m

Table 4.2 (cont.)

(54)	2970vs, 2922m, 2250w, 1416m, 1342w, 1262vs, 1178m, 1060vs, 866s, 816vs, 748m, 707m, 692m, 650m
(55)	2960s, 2898w, 2150m, 1442w, 1410m, 1258vs, 1054vs, 908s, 856m, 790vs, 754m, 696m, 682m, 658m
(56)	3060m, 2950s, 1592w, 1576w, 1462s, 1435s, 1408m, 1380s, 1190m, 1158s, 1075s, 1004m, 922w, 804s, 741s, 694s, 661m, 541w, 517m, 493m, 422w, 354w
(58)	3050w, 2925vs, 2848vs, 1967s, 1586w, 1568w, 1460s, 1437s, 1407w, 1376m, 1307w, 1260m, 1156m, 1060s, 800m, 738m, 688s, 653w
(60)	2950vs, 1590w, 1574w, 1460vs, 1412m, 1375s, 1260vs, 1157m, 1060vs, 862m, 802vs, 740m, 721m, 695m, 661w, 540w, 515w, 493w, 400m

Table 4.3 Infrared absorption data on the functional groups of cyclic and linear polysiloxanes

Compound	Infrared absorption	Infrared absorption frequency (cm^{-1})
(47)	(C=C)	1601m
(49)	(C=C)	1586m, 1572w
(50)	(C=C)	1600m
(52)	(C=C)	1586w
(53)	(C=C)	1602m
(54)	(C N)	2250w
(55)	(Si-H)	2150m

The infrared spectra of the ligand functionalised cyclic and linear polysiloxanes were very similar to their trisiloxane analogues with respect to absorption intensity and band position. The major absorptions of the polymers, which are a consequence of the siloxane backbone structure, were identified by comparison to those bands listed previously in Table 2.3, and those which were attributable to the ligating functional groups are summarised in Table 4.3.

The asymmetric SiOSi stretching vibration in the functionalised tri- and linear polysiloxanes was observed as a single broad absorption between 1100-1000 cm^{-1}, but for the cyclic siloxanes this band splits into two components, the positions of which are essentially independent of the other silicon substituents.[173] This was well illustrated in the cyclic vinyl (47) and bromo (48) siloxanes with peaks at 1083/1028 and 1100/1025 cm^{-1} respectively.

The infrared spectra of both the metallated cyclic (56) - (58) and linear polysiloxanes (59) - (64) were very similar to their respective model siloxane analogues, and in view of the relative insolubility of these samples in deuterated organic solvents which prevented ^{1}H and ^{13}C n.m.r. from being recorded, this technique was used exclusively to identify the metal carbonyl containing derivatives. The presence of the rhodium bonded carbonyl group in (58) and (61) was shown by strong bands at 1967 and 1964 cm^{-1} respectively, which compares with 1965 cm^{-1} for the analogous trisiloxane complex (31). It is interesting to note that polymeric complexes containing the Rh(CO)Cl moiety anchored through phosphine ligands have previously been reported to exhibit one to four carbonyl bands in their infrared spectra,[89] however, no conclusions to this were drawn by the authors.

The two strong carbonyl absorptions of the molybdenum tricarbonyl

complexed polysiloxane (63) were observed at 1969 and 1889 cm^{-1} and represent the A, and E modes respectively. These bands compare well with those of compound (38) which appear at 1973 and 1894 cm^{-1}.

The infrared spectrum of the polysiloxane supported osmium cluster was recorded in cyclohexane, and characteristic sharp metal carbonyl absorptions were seen at 2100w, 2072m, 2062s, 2049m, 2021vs, 2007s and 1982m cm^{-1}. These values are similar to those of the model complex $(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)H_2Os_3(CO)_{10}$ and are in similar positions to bands found for $H_2Os_3(CO)_{10}PPh_3$ by Deeming and Hasso.[171] Further comparisms were made with infrared spectra recorded for polystyrene and silica supported analogues synthesised by Freeman et al.[172] There was no evidence for any unreacted starting material, $H_2Os_3(CO)_{10}$, which has characteristic bands at 2076 and 1957 cm^{-1}.

For the polymer supported catalysts containing metal chloride moieties, absorptions due to the M-Cl stretch were not positively identified in the spectra of (56) - (58) and (59) - (62). In view of the low concentration of these entities compared to the siloxane polymer backbone, it is not surprising that these vibrations could not be identified positively, although in a number of spectra (especially those of cyclic metallated derivatives), weak shoulders in the far-infrared region were in the expected positions for M-Cl stretching vibrations.

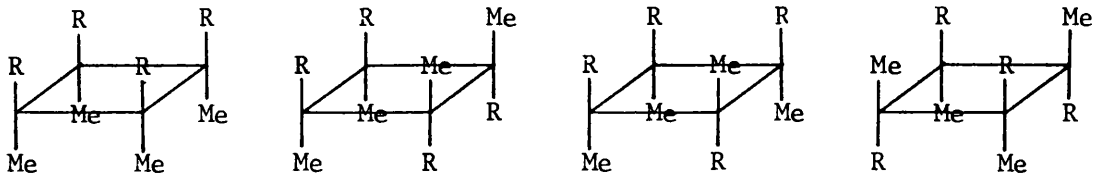
4.3.3 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

4.3.3a CYCLIC SILOXANES

^1H and ^{13}C n.m.r. spectra were recorded in deuterochloroform for the functionalised cyclic siloxanes (47 - (49), and spectral data has been listed in Table 4.4. The analysis of these spectra was a straightforward procedure since the individual molecules consist of one repeating unit,

$\left[SiMe(R)O\right]_4$, where R represents the ligating side chain.

The cyclic vinylsiloxane (47) exhibited resonances for C_1 and C_2 of the vinyl group at δ 136.27 and 133.40 respectively in its ^{13}C n.m.r. spectrum. On bromination, the C_1 and C_2 resonances were shifted to lower field at δ 38.59 and 33.39 respectively. Similarly, in the proton n.m.r. spectra the vinyl protons of (47) which were observed as a multiplet at δ 6.30 gave rise to two broad overlapping resonances centred at δ 4.50 and 4.27 for H_1 and H_2 respectively on addition of bromine. The cyclic siloxyphosphine (49) shows coupling between the ^{31}P nucleus and all of the carbon atoms in this compound with the exception of the SiMe group in the ^{13}C spectrum. The ^{1}H n.m.r. spectrum of (49) showed poorly resolved broad resonances for all of the protons, including the SiMe group which was observed as a broad singlet with fine structure, and no improvements were found on phosphorus decoupling. On comparison of the ^{1}H and ^{13}C spectra of (49) with those of the diphenylphosphine functionalised trisiloxane (26), no significant differences in chemical shifts were noted for structurally similar units found in each compound. Of the four possible structures which are illustrated for the arrangement of the methyl and ligating side chain about each silicon centre, structures (i) and (iv) would be expected to exhibit identical n.m.r. spectra, with the latter being thermodynamically favoured in view of the maximum separation between the groups.



(i) (ii) (iii) (iv)

Table 4.4 1H and 13C n.m.r. data for functionalised cyclic siloxanes

	SiMe	C1/H1	C2/H2	AROMATICS
(47)	0.52(12H, s)	6.30(12H, m)		
	-0.80	136.277.60	133.40	
(48)	1.18(12H, s)	4.50(4H, m)	4.27(8H, m)	
	-2.09	38.59	33.39	
(49)	0.07(12H, s)	0.66(8H, m)	2.04(8H, m)	7.21(40H, m)
	-1.12	13.41(d, 10.97)	21.53(d, 13.43)	139.55(d, 14.65), 133.46(d, 18.31)

4.3.3b LINEAR POLYSILOXANES

The linear polysiloxanes (50) - (55) were easily miscible with deuterated organic solvents ($CDCl_3$, $(CD_3)_2CO$, C_6D_6), and this enabled ^{13}C n.m.r. spectra to be recorded without long acquisition times. For all of the spectra, dichloromethane was used as an external reference (δ 5.3) in preference to tetramethylsilane (TMS) to avoid overlap with the ($SiMe_2O$) resonances. The ^1H and ^{13}C spectral data for the above polysiloxanes are listed in Table 4.5.

The recorded spectra for each polysiloxane were very similar to those of their respective trisiloxane analogues with no significant differences in chemical shifts for chemically identical groups found in both classes of compound. Consequently, there is no further discussion of this data.

From the ^1H n.m.r. spectra, analysis of the relative integrals for individual resonances was used to evaluate the mean average spacing of functional groups with respect to the silanone moiety $(SiMe_2O)_x$ in each individual polysiloxane. This was easily achieved since the silanone and functional group resonances were found to be well separated in all of the recorded spectra. The bromo (51) and phosphine (52) functionalised polymers derived from the polyvinylsiloxane (50) both had an average functional group separation of eight ($SiMe_2O$) units, which indicated that there had been no obvious degradation or structural rearrangement on chemically modifying (50) with either hydrogen bromide, or with diphenylphosphine under ultraviolet irradiation. The arene (53), nitrile (54) and hydrido (55) functionalised polymers were found to have ligating side chains at an average of every six, five and twelve silanone groups respectively.

Table 4.5 1H and 13C n.m.r. data for functionalised polysiloxanes

	SiMe	Me_3SiO	C1/H1	C2/H2	OTHERS	AROMATICS
(50)	0.22(3H, s)	0.15(48H, s)	5.96(3H, m)			
	0.00	1.62	137.60	133.48		
(51)	0.12(3H, s)	0.12(48H, s)	1.40(2H, m)	3.54(2H, m)		
	1.00	1.00	24.43	29.12		
(52)	0.18(3H, s)	0.18(48H, s)	0.68(2H, m)	2.06(2H, m)		7.16(10H, m)
	-0.68	0.94	12.88(d, 11.04)	20.69(d, 13.43)		138.87(d, 14.6), 132.64(d, 17.1) 130.63, 128.28(d, 3.51)
(53)	0.15(3H, s)	0.15(30H, s)	0.96(2H, m)	2.76(2H, m)	7.30(5H, s)	
	-0.47	1.05	19.53	29.12	144.99, 128.25, 127.71, 125.44	
(54)	0.00(3H, s)	0.00(30H, s)	0.58(2H, m)	2.27(2H, m)		
	1.57	1.57	20.31	20.81	120.10(CN)	
(55)	0.24(3H, s)	0.24(72H, s)			4.70(1H, s)	

4.4 MISCELLANEOUS REACTIONS

By an analogous procedure to that described previously for aluminium chloride catalysed Friedal Crafts reactions, attempts to produce $\left[SiMe(CH_2CH_2Ph)O\right]_4$ by reacting the cyclic vinylsiloxane (47) with benzene were unsuccessful. In all cases infrared and ^1H n.m.r. spectroscopic analysis showed that no addition reaction had occurred, and these results are in accord with those found for the analogous reaction using vinylsiloxane (17) and benzene.

Although the functionalised cyclotetrasiloxane (48) was readily formed by bromination of (47), attempts to synthesise a monobromo- functionalised derivative by the organic peroxide catalysed anti-Markovnikoff addition of hydrogen bromide to (47), using a similar procedure to that employed for preparing (24) , failed to produce the desired product. In each attempt, the crude product isolated after pumping off residual hydrogen bromide in vacuo was an extremely air-sensitive colourless oil which fumed when exposed to the atmosphere. This product was of insufficient volatility to be distilled under reduced pressure, and in view of the sensitivity of this compound, no further purification procedures were tried. A ^{13}C n.m.r. spectrum showed an additional resonance at δ 4.01 besides those at δ -0.81, 22.86 and 27.80 which are assigned to SiMe, $SiCH_2$, and CH_2Br groups respectively.

Reactions of (48) with NaC_5H_5, LiC_5H_5 and $LiPPh_2$ failed to yield any pure products which were functionalised with either the cyclopentadienyl or diphenylphosphine moieties. Only intractable gums consisting of mixtures of products were formed in each instance. Similar observations were made on reacting NaC_5H_5 or $LiPPh_2$ with the bromofunctionalised trisiloxane (24).

4.5 SYNTHETIC PROCEDURES

4.5.1 SYNTHESES OF FUNCTIONALISED CYCLOSILOXANES

PURIFICATION OF $\left[SiMe(CH{=}CH_2)O\right]_4$ (47)

Distillation of a mixture of cyclic vinylsiloxanes (Dow Corning Ltd.) having a general formula of $\left[SiMe(CH{=}CH_2)O\right]_n$ (n = 3 to 8) yielded $\left[SiMe(CH{=}CH_2)O\right]_4$ (47), b.p. 222° (747 mmHg). (Found: C, 41.51; H, 6.76. $C_{12}H_{24}O_4Si_4$ requires C, 41.86; H, 6.97%), which was found to be analytically pure from mass spectrometry studies.

PURIFICATION OF $(SiMe_2O)_4$

Distillation of a mixture of cyclic dimethylsiloxanes (Dow Corning Ltd.) of formula $(SiMe_2O)_n$ (n = 3 to 8) yielded $(SiMe_2O)_4$ b.p. 175° (760 mmHg) as the major component of the siloxane mixture. Mass spectrometry was again used as a criterion of purity.

$\left[SiMe(CHBrCH_2Br)O\right]_4$ (48)

To (47) (3.20 g, 9.30 mmol) in CCl_4 (5 ml) was added bromine (7 g, 44.0 mmol) dropwise with stirring at ambient temperature. The mixture was warmed to 60°C and the progress of the reaction monitored by infrared spectroscopy. After cooling the mixture was heated *in vacuo* to eliminate any volatiles, leaving (48) as a golden viscous oil (9.06 g, 99%). (Found: C, 14.54; H, 2.41; Br, 63.09. $C_{12}H_{24}Br_8O_4Si_4$ requires C, 14.64; H, 2.44; Br, 65.00%).

$\left[SiMe(CH_2CH_2PPh_2)O\right]_4$ (49)

A mixture of (47) (1.50 g, 4.36 mmol) and Ph_2PH (3.24 g, 17.40 mmol) was sealed under a N_2 atmosphere in a 25 ml thick-walled Pyrex tube. The tube was irradiated for 48h while the contents were continuously stirred.

Distillation without decomposition was not possible, and the colourless glass appeared analytically pure after pumping in vacuo (0.01 mmHg), and there was no spectroscopic evidence for unreacted starting materials (4.6 g, 97%). (Found: C, 65.22; H, 6.12; P, 11.59. $C_{60}H_{68}O_4P_4Si_4$ requires C, 66.17; H, 6.25; P, 11.39%).

4.5.2 SYNTHESES OF METAL-COMPLEXED CYCLOSILOXANES

$\left[SiMe(CH_2CH_2PPh_2)O\right]_4Pd_2Cl_4$ (56)

To $PdCl_2(MeCN)_2$ (0.065 g, 0.25 mmol) in CH_2Cl_2 (15 ml) was added (49) (0.136 g, 0.125 mmol) in CH_2Cl_2 (2 ml) dropwise with rapid stirring at ambient temperature. The red colour was discharged immediately on addition to produce a golden yellow solution which was stirred for 2h. After evaporation in vacuo, the yellow solid was recrystallised from dichloromethane/hexane (0.17 g, 94%) (Found: C, 49.80; H, 5.05. $C_{60}H_{68}Cl_4O_4P_4Pd_2Si_4$ requires C,49.93; H, 4.71%).

$\left[SiMe(CH_2CH_2PPh_2)O\right]_4Pt_2Cl_4$ (57)

To $PtCl_2(MeCN)_2$ (0.147 g, 0.42 mmol) in CH_2Cl_2 (20 ml) was added (49) (0.23 g, 0.21 mmol) in CH_2Cl_2 (3 ml) dropwise with stirring at ambient temperature. The mixture was stirred for 15h at this temperature before isolating the product (as above) as a white solid (0.30 g, 90%). Found: C, 43.38; H, 4.72; Cl, 8.50. $C_{60}H_{68}Cl_4O_4P_4Pt_2Si_4$ requires C, 44.44; H, 4.19; Cl, 8.76%).

$\left[SiMe(CH_2CH_2PPh_2)O\right]_4Rh_2(CO)_2Cl_4$ (58)

To $\left[Rh(CO)_2Cl\right]_2$ (0.084 g, 0.216 mmol) in benzene (12 ml) was added a solution of (49) (0.235 g, 0.216 mmol) in benzene (8 ml). The mixture was refluxed for 5h after which ν(CO) of the starting material had

disappeared. The solution was cooled and the solvent evaporated under reduced pressure to give an orange solid which was purified by recrystallising from dichloromethane and hexane (0.17 g, 52%). (Found: C, 38.4; H, 4.32. $C_{62}H_{68}Cl_4O_6P_4Rh_2Si_4$ requires C, 52.30; H, 4.78; Cl, 5.00%). Analysis results were consistently low for independently prepared samples, and apart from incomplete combustion occurring in the analyser, we offer no explanation for these anomalous results.

4.5.3 SYNTHESES OF FUNCTIONALISED POLYSILOXANES

$Me_3SiO\left[(SiMe_2O)_8SiMe(CH=CH_2)O\right]_nSiMe_3$ (50).

To a stirred mixture of $\left[SiMe(CH=CH_2)O\right]_4$ (7.26 g, 21.10 mmol), $(SiMe_2O)_4$ (25.0 g, 84.40 mmol) and $(SiMe_3)_2O$ (0.526 g, 3.24 mmol) was added dropwise CF_3SO_3H (0.032 g). The mixture was heated to 74°C and maintained at this temperature for 62h, whereupon the siloxanes present had reached equilibrium as indicated by the solution having a constant viscosity. The catalyst was neutralised by addition of dimethylformamide (0.5 x weight of TFMSA). After stirring for 1h the solution was cooled to ambient temperature and filtered using dicalite filter aid. The filtrate was carefully heated under reduced pressure to remove volatiles and unreacted $(SiMe_2O)_4$ leaving the product as a colourless oil (29.70 g, 90%). (Found: C, 33.17; H, 7.97. $C_{19}H_{54}O_9Si_9$ requires C, 33.62; H, 7.96%). Similar synthetic procedures were used to prepare the linear polyvinylsiloxanes (50a) - (50e), whose physical data are listed in Table 4.6.

Table 4.6 Physical data for polyvinylsiloxanes (50a) - (50e)

Polymer	$[SiMe(CH=CH_2)O]_4$	$(SiMe_2O)_4$	$(SiMe_3)_2O$	T(°C)	mol %($CH=CH_2$)	M_w*
(50a)	3.96g	13.65g	0.287g	74	19.7	20000
(50b)	4.36g	15g	0.158g	74	19.8	26300
(50c)	4.35g	15g	0.164g	64	19.8	28700
(50d)	2.90g	15g	0.148g	64	14.0	32400
(50e)	4.35g	15g	0.093g	64	19.9	38600

(*M_w mean average molecular weight)

$Me_3SiO[(SiMe_2O)_8SiMe(CH_2CH_2Br)O]_nSiMe_3$ (51)

Anhydrous HBr was passed through a solution of (50) (3.50 g, 0.166 mmol) in CCl_4 (5 ml) containing benzoyl peroxide (ca 0.10 g) at 40°. The progress of reaction was followed using infrared spectroscopy by monitoring the disappearance of (C=C) of the starting material. On completion of addition the mixture was cooled then filtered using dicalite filter aid to yield the product as a mobile, analytically pure, colourless oil (3.70 g, 94%). (Found: C, 30.81; H, 712; Br, 11.44. $C_{19}H_{55}BrO_9Si_9$ requires C, 30.08; H, 7.25; Br, 10.42%).

$Me_3SiO[(SiMe_2O)_8SiMe(CH_2CH_2PPh_2)O]_nSiMe_3$ (52)

A mixture of (50) (5.00 g, 7.38 mmol $CH=CH_2$) and $PHPh_2$ (1.44 g, 7.74 mmol)

was sealed under a N_2 atmosphere in a 25 ml thick-walled Pyrex tube. The tube was irradiated for 48h with a 400-W mercury lamp while the contents were continuously stirred. On completion of the reaction the product was isolated as a viscous white oil which appeared analytically pure from spectroscopic measurements. (Found: C, 40.00; H, 7.67. $C_{31}H_{65}O_9PSi_9$ requires C, 43.00; H, 7.52%).

$Me_3SiO\left[(SiMe_2O)_6SiMe(CH_2CH_2Ph)O\right]_nSiMe_3$ (53)

To $SiMeCl_2(CH_2CH_2Ph)$ (3.00 g, 13.7 mmol) cooled to 0°C was added dropwise over 0.25h H_2O (0.493 g, 27.4 mmol). The mixture was stirred for 1h with a stream of N_2 bubbled through the solution to displace hydrogen chloride gas. After addition of $(SiMe_2O)_4$ (6.05 g, 20.4 mmol) and $(SiMe_3)_2O$ (0.074 g, 0.45 mmol) the mixture was allowed to warm to ambient temperature and CF_3SO_3H (0.009 g) added to catalyse the polymerisation. The mixture was heated to 65°C and maintained at this temperature until equilibriation had occurred, after which the catalyst was neutralised with DMF (0.0045 g). Following stirring at this temperature for 1h, the solution was cooled, diluted with toluene (50 ml) and dried over anhydrous Na_2SO_4. After filtering, the solvent and volatile by-products were removed by carefully distilling under reduced pressure to yield (53) as a colourless oil (2.95 g). (Found: C, 41.96; H, 7.81. $C_{19}H_{42}O_7Si_7$ requires C, 41.44; H, 7.89%).

$Me_3SiO\left[(SiMe_2O)_5SiMe(CH_2CH_2CH_2CN)O\right]_nSiMe_3$ (54)

By a similar procedure, (54) was prepared using $SiMeCl_2(CH_2CH_2CH_2CN)$ (2.00 g, 10.9 mmol), H_2O (0.40 g, 21.8 mmol), $(SiMe_2O)_4$ (5.73 g, 19.3 mmol), $(SiMe_3)_2O$ (0.044 g, 0.27 mmol) and CF_3SO_3H (0.008 g). Unreacted

$(SiMe_2O)_4$ was removed from the higher polymers by preparative gel permeation chromatography. The product (54) was isolated as a colourless oil (5.4 g). (Found: C, 34.60; H, 8.14. $C_{15}H_{39}NO_6Si_6$ requires C, 36.21; H, 7.84%).

$Me_3SiO\left[(SiMe_2O)_{12}SiMe(H)O\right]_nSiMe_3$ (55)

The title polysiloxane was prepared by an analogous procedure to (53) using $SiMeCl_2(H)$ (2.59 g, 22.5 mmol), H_2O (0.81 g, 45.0 mmol) $(SiMe_2O)_4$ (10.0 g, 33.7 mmol), $(SiMe_3)_2O$ (0.091 g, 0.56 mmol) and CF_3SO_3H (0.013 g). The mixture was equilibriated at 65°C. (11.8 g) (Found: C, 30.94; H, 7.83. $C_{25}H_{76}O_{13}Si_{13}$ requires C, 31.64; H, 8.01%).

4.5.4 SYNTHESES OF METAL-COMPLEXED POLYSILOXANES

$\left\{Me_3SiO\left[(SiMe_2O)_8SiMe(CH_2CH_2PPh_2)O\right]_nSiMe_3\right\}_2PdCl_2$ (59)

To $PdCl_2(MeCN)_2$ (0.0374 g, 0.0144 mmol) in CH_2Cl_2 (12 ml) was added (52) (0.25 g, 0.029 mmol P) in CH_2Cl_2 (3 ml). The yellow solution was stirred at ambient temperature overnight, after which, TLC (CH_2Cl_2/silica) showed no evidence for unreacted $PdCl_2(MeCN)_2$. The solution was filtered and the solvent evaporated *in vacuo* to give the product as an orange-yellow gum (0.25 g, 90%) (Found: C, 38.60; H, 6.70. $C_{31}H_{65}ClO_9PPd_{\frac{1}{2}}Si_9$ requires C, 39.05; H, 6.82%).

$\left\{Me_3SiO\left[(SiMe_2O)_8SiMe(CH_2CH_2PPh_2)O\right]_nSiMe_3\right\}_2PtCl_2$ (60)

By employing a similar procedure to that above, the title compound was prepared using $PtCl_2(MeCN)_2$ (0.06 g, 0.17 mmol), (52) (0.30 g, 0.035 mmol P) and CH_2Cl_2 (20 ml). The product was isolated as a lemon yellow solid

(0.31 g, 89%). (Found: 34.00; H, 6.52. $C_{31}H_{65}ClO_9PPt_{\frac{1}{2}}Si_9$ requires C, 37.31; H, 6.52%).

$\left\{Me_3SiO\left[(SiMe_2O)_8SiMe(CH_2CH_2PPh_2)O\right]_nSiMe_3\right\}_2Rh(CO)Cl$ (61)

A mixture of $Rh(CO)_2Cl_2$ (0.045 g, 0.011 mmol) and (52) (0.40 g, 0.046 mmol P) in benzene (20 ml) were refluxed for 4h. The solution was cooled and the solvent evaporated in vacuo to yield an orange-brown fibrous gum. The gum was triturated in hexane to give (61) as an orange-brown solid (0.38 g, 86%) (Found: C, 39.42; H, 6.89; P, 3.20. $C_{63}H_{130}ClO_{19}P_2RhSi_{18}$ requires C, 39.91; H, 6.86; P, 3.27%).

$\left\{Me_3SiO\left[(SiMe_2O)_8SiMe(CH_2CH_2PPh_2)O\right]_nSiMe_3\right\}_3RhCl$ (62)

A mixture of $RhCl(C_2H_4)_2{}_2$ (0.015 g, 0.0038 mmol) and (52) (0.20 g, 0.23 mmol P) in benzene (25 ml) were stirred overnight at ambient temperature. After filtering the solution, TLC (benzene/silica) of the filtrate showed no indication of unreacted $RhCl(C_2H_4)_2{}_2$. Evaporation of the solvent under reduced pressure yielded (62) as a red-brown fibrous solid (0.18 g, 86%) (Found: C, 39.20; H 7.14. $C_{93}H_{195}ClO_{27}P_3RhSi_{27}$ requires C, 40.86; H, 7.14%).

$\left\{Me_3SiO\left[(SiMe_2O)_6SiMe(CH_2CH_2Ph)O\right]_nSiMe_3\right\}Mo(CO)_3$ (63)

To (53) (0.30 g, 0.5 mmol Ph) and $Mo(CO)_3(py)_3$ (0.206 g, 0.5 mmol) in Et_2O (65 ml) was added $BF_3.OEt_2$ (0.213 g, 0.5 mmol) dropwise. The mixture was stirred at ambient temperature for 2h before diluting with hexane (80 ml), washing with water (3 x 100 ml) and separating. The organic phase was dried over anhydrous Na_2SO_4, filtered and the solvent

evaporated *in vacuo* to yield (63) as a yellow viscous gum (0.21 g, 54%). The metallated polymer was identified by infrared spectroscopy.

$\{Me_3SiO[(SiMe_2O)_8SiMe(CH_2CH_2PPh_2)O]_nSiMe_3\}\{H_2Os_3(CO)_{10}$ (64)

(52) (0.066 g, 0.0076 mmol P) and $H_2Os_3(CO)_{10}$ (0.065 g, 0.0076 mmol) in hexane (25 ml) were stirred for 13h at ambient temperature. The yellow solution was filtered and evaporated to dryness *in vacuo* yielding a golden coloured gum. The gum was washed with hexane (*ca* 2 ml), filtered and dried *in vacuo* (0.11 g, 84%). This metallated polymer was characterised by infrared spectroscopy only.

CHAPTER FIVE

CATALYTIC STUDIES ON POLYSILOXANE SUPPORTED METAL CATALYSTS

5.1 INTRODUCTION

The group VIII transition metals rhodium(I), palladium(II) and platinum(II) in combination with tertiary phosphine ligands have been used extensively as homogeneous catalysts, and numerous reports summarising new and well established applications of these materials have appeared in the literature over recent years.[174] Of the metallated tri- and polysiloxanes described previously, those derived from phosphine functionalised siloxanes have proved to be the most stable towards air and organic solvents, and consequently a number of compounds containing group VIII metal entities appeared suitable for testing for catalytic activity. In view of the limited time available studies were confined to olefin hydrogenation and hydrosilylation reactions. These two classes of reaction can be represented by the following general equations:

Hydrogenation $\rangle C{=}C\langle + H_2 \xrightarrow{\text{catalyst}} \rangle CH{-}CH\langle$ (65)

Hydrosilylation $R_3SiH + R'CH{=}CH_2 \xrightarrow{\text{catalyst}} \begin{cases} R'CH_2CH_2SiR_3 \\ CH_3CHR'SiR_3 \end{cases}$ (66)

Many active hydrogenation catalysts have originated from metal complexes such as $RhCl(PPh_3)_3$, $\left[RhCl(C_2H_4)_2\right]_2$ and $RhCl_3$ in combination with phosphinated organic polymers and inorganic supports. For example,

Grubbs and Kroll have made extensive studies on polystyrene supported $RhCl(PPh_3)_3$ as an olefin hydrogenation catalyst. As well as rhodium based catalysts, many palladium(II) and platinum(II) systems including H_2PtCl_6, $PdCl_2$ and $PdCl_2(PPh_3)_2$ have been supported on functionalised matrices and subsequently used to good effect in hydrosilylation reactions. For example, phosphinated inorganic oxides complexed with chloroplatinic acid have proved to be effective catalysts for hydrosilylating terminal olefins with simple silanes.

5.2 CATALYTIC METHODS

5.2.1 HYDROGENATION OF OLEFINS

The catalysts which have been tested for activity in olefin hydrogenation reactions have included $PdCl_2L_2$ (31), $RhClL_3$ (35), where L = $(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)$ (26), $\left\{Me_3SiO\left[(SiMe_2O)_8SiMe(CH_2CH_2PPh_2)O\right]_n SiMe_3\right\}_2PdCl_2$ (59) and $\left\{Me_3SiO\left[(SiMe_2O)_8SiMe(CH_2CH_2PPh_2)O\right]_n SiMe_3\right\}_3RhCl$ (62) as neat samples. $RhCl(PPh_3)_3$, Wilkinson's complex, was used as a reference for qualitatively assessing the catalytic reactivity of our systems.

The olefin hydrogenation reactions have been assessed in two ways. Initially, a series of experiments on an n.m.r. tube scale at varying temperatures were carried out to establish whether any of the above systems have catalytic activity. The olefin substrates cyclohexene, 1-octene and styrene have been used whilst the solvent systems have included benzene, d_6-benzene/ethanol, d_6-acetone, and d_6-acetone/ethanol. Ethanol was present as a co-solvent in relatively small quantities compared to the volumes of deuterated solvent used. The experimental method consisted of placing the olefin, catalyst and solvent(s) into a

5 mm diameter n.m.r. tube and saturating the mixture with dry hydrogen gas. After tightly stoppering, the tube was immersed into a water bath fitted with a thermostatic control. At periodic time intervals the tube was removed from the bath, cooled to ambient temperature and the contents analysed by proton n.m.r. spectroscopy for alkane product formation. Table 5.1 summarises the catalysts, solvents, substrates and temperatures used for the n.m.r. tube scale experiments.

Table 5.1 Summary of n.m.r. tube scale hydrogenation experiments

Substrate	Solvent	Catalyst	Temperature(^{o}C)
cyclohexene	benzene	$RhCl(PPh_3)_3$	rt and 35
cyclohexene	benzene	(35)	rt and 35
cyclohexene	d_6-benzene	(31)	rt
styrene	d_6-acetone	(31)	rt
cyclohexene	d_6-benzene/ethanol	(31)	35, 50 and 60
cyclohexene	d_6-benzene/ethanol	(35)	50 and 60
cyclohexene	d_6-benzene/ethanol	(59)	60
cyclohexene	d_6-benzene/ethanol	(62)	60
1-octene	d_6-benzene/ethanol	(31)	60

Based on the results of these qualitative tests a number of larger scale experiments at elevated temperatures using both (59) and (62) as catalysts at concentrations of 4.3×10^{-6} mol Rh and 6.5×10^{-6} mol Pd respectively (with these values being calculated on the assumption that the phosphine

polymer (52) was fully metallated in both cases). The hydrogenation reactions were carried out on cyclohexene in benzene/ethanol mixtures at 50 and 60°C, and for allyl alcohol in benzene alone at 60°C using both of the above polymer supported catalysts. The progress of each reaction was monitored by gas liquid chromatography, and entailed comparing the relative peak heights of the substrate olefin to the product alkane, whose retention times were sufficiently different for their peaks to be well separated. The apparatus consisted of a small one-necked flask which contained a mixture of the substrate, solvent and catalyst which had been previously degassed with nitrogen and then saturated with hydrogen. The quantities of these reagents were kept constant on a weight to weight basis for each individual experiment. The flask was fitted with a septum cap through which a gas inlet tube from a hydrogen gas reservoir could be introduced. The reaction temperature was kept constant by use of a thermostated water bath, and at frequent intervals samples were withdrawn from the flask and analysed.

5.2.2 HYDROSILYLATION REACTIONS

The procedure used for testing $PdCl_2L_2$ (31), $PtCl_2L_2$ (32), $Rh(CO)ClL_2$ (34) and $RhClL_3$ (35), where L = (26) and $\left\{Me_3SiO\left[(SiMe_2O)_8SiMe(CH_2CH_2PPh_2)O\right]_n SiMe_3\right\}_2Rh(CO)Cl$ (61) as hydrosilylation catalysts was based on the method described by Chalk[175] for $Rh(CO)Cl(PPh_3)_2$. Initially a range of hydrosilylation reactions between olefins and Si-H containing materials using all three catalysts were carried out, and from the results of these tests a number of similar reactions under controlled conditions with gas chromatographic product analysis were performed using (34) and its polysiloxane supported analogue (61). The Si-H containing siloxanes used were $(Me_3SiO)_2SiMe(H)$ (22) and its polymeric analogue

$Me_3SiO\left[(SiMe_2O)_{12}SiMe(H)O\right]_nSiMe_3$ (55), with the silane $(EtO)_3SiH$ being used for a single reaction. The range of terminal olefins used included 1-hexene $CH_3(CH_2)_3CH=CH_2$, 1-octene $CH_3(CH_2)_5CH=CH_2$ and 1-decene $CH_3(CH_2)_7CH=CH_2$, together with 4-vinylpyridine in just one reaction.

All of the hydrosilylation reactions were effected under a nitrogen atmosphere to prevent hydrolysis of the Si-H bond by atmospheric moisture. The initial investigative procedure entailed mixing the catalyst, olefin and Si-H containing siloxane together and heating under gentle reflux for 1 hour. The reflux temperature was governed by the boiling point of the olefin used as this was the most volatile component present. After cooling to ambient temperature, any excess olefin was evaporated by pumping in vacuo and the residue was then distilled under reduced pressure to isolate the hydrosilylation addition product. The products were analysed by infrared and nuclear magnetic resonance spectroscopy, with further characterisation by elemental analyses. With the exception of the polymer supported catalyst (61), all of the catalysts used were soluble in the olefin/siloxane mixtures, and the use of organic solvents for solubility purposes was not necessary.

The hydrosilylations which were monitored using gas chromatographic analysis, were carried out in order to establish basic kinetic data for this type of reaction. The procedure involved introducing a solution of the catalyst in the olefin substrate to a small flask fitted with a septum cap containing a mixture of the olefin and siloxane. The contents were maintained at a constant temperature in a thermostatically controlled water bath accurate to $\pm$ 0.5°C.

For experiments using (61), which was insoluble in the substrate olefin, the catalyst was introduced and placed onto the wall of the reaction

flask above the liquid level. When the solution temperature had been raised and kept at a constant temperature, the flask contents were shaken to wash the catalyst into the solution, and the reaction subsequently monitored.

One of the major advantages of using a polymer supported catalyst as opposed to a homogeneous system is the ease of separation from the product mixture. For the reaction of (22) with 1-hexene using (61), the catalyst was freed from the product mixture by filtering after slurrying with n-hexane. In the case of the equivalent hydrosilylation reaction using $\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]_2Rh(CO)Cl$ (34), the catalyst remained homogeneously dispersed within the polysiloxane product and could not be separated by simple filtration techniques.

5.3 RESULTS AND DISCUSSION

5.3.1 HYDROGENATION STUDIES

The catalysts (35), (59) and (62) all showed catalytic activity for the hydrogenation of simple olefin substrates, even though there were only trace conversions with the palladium metallated siloxane (31). The best hydrogenation result was found for the rhodium metallated siloxyphosphine (35) with a ca 9% conversion of cyclohexene to cyclohexane in d_6-benzene/ethanol under the conditions described above.

For the n.m.r. tube scale studies, a ^1H n.m.r. spectrum of the system under test gave a rapid method of determining product formation. In the case of cyclohexene to cyclohexane reductions, the alkane product gave a single sharp diagnostic resonance at δ 1.44. By comparing the relative integrals of the substrate olefin to the alkane reduction product, a semi-quantitative hydrogenation conversion could be attained.

The results of both the n.m.r. and larger scale experiments indicated that a small quantity of ethanol as a co-solvent was necessary for any of the metallated siloxanes to show hydrogenation activity, and that temperatures of 35°C and above were required. However, the ethanol present eventually promoted leaching of metal from the catalyst, especially with rhodium where a black solid was deposited in solution with an accompanying loss of catalytic activity as shown by gas chromatographic analysis, where the ratio of substrate to product peaks did not change with time. This was very evident at temperatures of 50°C and above. The larger scale reactions were not quantitatively analysed in view of the low concentrations of reduction products formed. For the experiment using allyl alcohol in benzene with the polysiloxane supported rhodium catalyst (62), the initial hydrogenation activity was relatively high in comparison to other reductions, but the catalyst soon darkened after 1 hour with a black solid precipitating from the solution which was evidence of metal leaching. There was no analogous hydrogenation reaction for the polymer supported palladium catalyst. The reference catalyst $RhCl(PPh_3)_3$, which gave a *ca* 12% conversion of cyclohexene to cyclohexane in d_6-benzene/ethanol, was a superior hydrogenation catalyst compared to our metallated siloxane systems, but this too appeared to suffer from leaching at elevated temperatures as has been noted previously.[89] In hydrogenation studies by Conan *et al*[92] using polyphenylsiloxane on silica supported catalysts, the authors also found that the presence of ethanol caused a decrease in catalytic activity during use although the deactivation was not as pronounced when compared to an analogous homogeneous catalyst in alcohols.[176]

5.3.2 HYDROSILYLATION STUDIES

The catalysts $Rh(CO)ClL_2$ (34), $RhClL_3$ (35) (where L = (26)) and

$\left\{Me_3SiO\left[(SiMe_2O)_8SiMe(CH_2CH_2PPh_2)O\right]_nSiMe_3\right\}_2Rh(CO)Cl$ (61) were successfully used in a range of hydrosilylation reactions between terminal olefins and Si-H containing compounds. However, no catalytic activity was noted for the model complexes (31) and (32) even under forcing conditions and reaction times of up to 24 hours. The reactions between 1-hexene, 1-octene or 1-decene with (22) using either (34) or (61) as catalyst can be represented by the following equation (67)

$$(Me_3SiO)_2SiMe(H) + CH_3(CH_2)_xCH{=}CH_2 \xrightarrow{\text{catalyst}} (Me_3SiO)_2SiMe(CH_2)_{x+2}CH_3 \quad (67)$$

where x = 3, 5 or 7 to give products (65), (66) and (67) respectively as listed with a summary of other hydrosilylation reactions in Table 5.2.

Table 5.2 Summary of hydrosilylation reactions

Si-H compound	Olefin	Catalyst	Product
(22)	1-hexene	(34) or (61) or (35)	(65)
(22)	1-octene	(34) or (61)	(66)
(22)	1-decene	(34) or (61)	(67)
(55)	1-hexene	(34) or (61)	(68)
$(EtO)_3SiH$	1-hexene	(35)	(69)
(22)	4-vinylpyridine	(34)	(25)

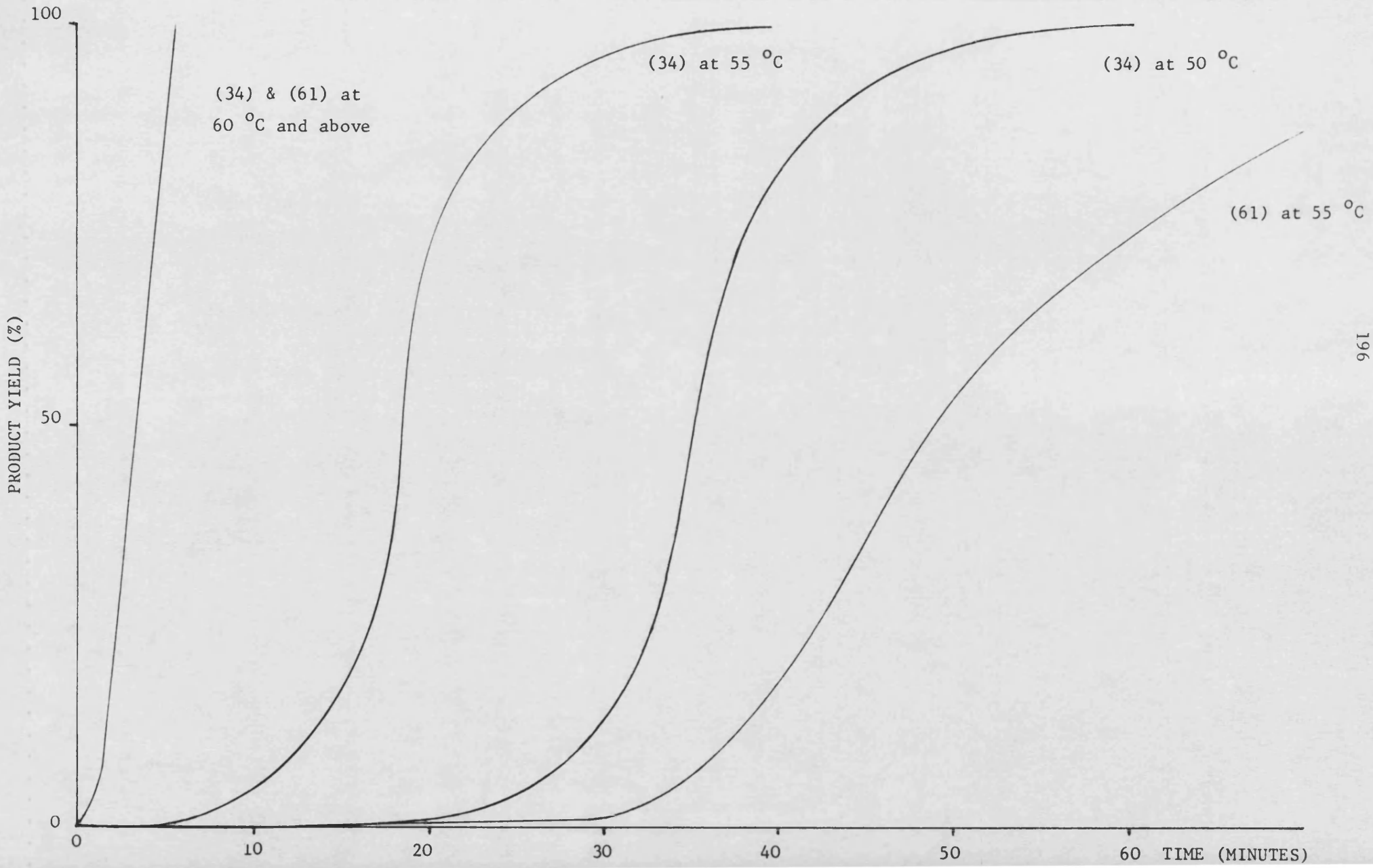
The products (65), (66), (67) and (69) were all isolated in yields of over 68% as colourless oils having sharp boiling points. In each case a single terminal addition product was formed, and this was confirmed by ^{1}H and ^{13}C n.m.r. spectroscopy which provided no evidence for CH or CH_3 moieties resulting from internal addition between Si-H and ($-CH=CH_2$). The products were also devoid of unreacted (22) with no (Si-H) resonance at δ 5.10 or ν(Si-H) absorption at 2160 cm^{-1} being found in the ^{1}H n.m.r. and infrared spectra respectively. Table 5.3 lists ^{1}H and ^{13}C n.m.r. chemical shift data for compounds (65) - (67) and (69).

From the temperature controlled experiments monitored by g.c. reactions using (34) and (61) as catalyst with 1-hexene, 1-octene or 1-decene as olefin substrate at a temperature of 60°C or above were found to be complete with 100% product formation within a few minutes. However, no reaction was found for any of these systems at ambient temperature over three days. On restricting our studies to $(Me_3SiO)_2SiMe(H)$ (22) and 1-hexene, hydrosilylation was found to occur slowly at 40°C using the model catalyst (34) but not for the polymer supported version. This latter catalyst began to show activity at 55°C after a short induction period of ca 15-20 minutes. Figure 5.1 shows graphs of product yield verses time of reaction for this hydrosilylation using both catalysts at constant temperatures. With the exception of the hydrosilylations at 60°C and above, the general shapes of the curves in Figure 5.1 showed similar characteristics, with each reaction having an induction interval prior to a short period where the reactants were consumed relatively quickly to give the product siloxane in high yield. The induction periods could represent the time taken to form an active six-coordinated intermediate about a rhodium centre which is an essential feature of the catalytic reaction. The occurrence of induction periods has been

Table 5.3 1H and 13C n.m.r. data for hydrosilylation reaction products

	$OSiMe_3$	SiMe	$(CH_2)_\alpha$	CH_3	OTHERS
(65)	0.27(18H, s) 1.97	0.20(3H, s) -0.09	0.40 - 1.70(10H, m) 33.23, 31.98, 23.37, 22.88, 17.90	1.05(3H, m) 14.27	
(66)	0.25(18H, s) 1.98	0.21(3H, s) -0.13	0.50 - 2.00(14H, m) 33.51, 32.21, 29.61, 23.32, 22.78, 17.85	1.07(3H, m) 14.22	
(67)	0.18(18H, s) 1.82	0.08(3H, s) -0.27	0.53(2H, m), 1.35(16H, s) 33.35, 32.05, 29.77, 29.50, 23.22, 22.78 17.74	0.97(3H, m) 14.06	
(69)			0.50 - 1.70(10H, m) 32.67, 31.37, 22.59, 22.43, 10.29	1.00(3H, m) 13.76	3.84(6H, q), 1.30(9H, t) 58.02(OCH_2), 18.04(CH_3)

Figure 5.1 Graphs of product yield verses time for hydrosilylation reactions between $(Me_3SiO)_2SiMe(H)$ and 1-hexene



similarly found by Marciniec et al[91] for the hydrosilylation of 1-hexene by triethoxysilane, and they comment on their temperature independence.

The model complex (34) was found to have superior activity over the polymer supported catalyst (61) at lower temperatures.This may be attributable to the greater solubility of (34) in the reaction mixtures used, and it was noted that when (61) was used polymeric material was frequently washed onto the walls of the flask above the liquid level and consequently was not able to take part in the reaction. In the course of reactions conducted at 60°C or above using (34) as catalyst, the solutions slowly darkened with a finely divided black solid being deposited. This was caused by leaching of rhodium metal from the catalyst, as observed in other rhodium systems by previous workers.[90] Although oxygen was excluded from the reactor as much as possible, the presence of trace amounts would have probably aided the leaching mechanism. No such leaching process was found for the polysiloxane supported catalyst (61) used under similar conditions, which indicates a stability difference between the two systems.

From one hydrosilylation reaction between (22) and 1-hexene using (61), the catalyst was recovered as outlined previously, and was further used in a similar hydrosilylation reaction to give compound (65) in 55% yield. This demonstrated that the polymer supported catalyst was still active for hydrosilylation reactivity compared to the analogous model complex whose metal content was leached out after one such reaction under identical conditions

The hydrosilylation reaction method was extended to couple an Si-H containing polysiloxane (55) with 1-hexene. This was successfully achieved at 60°C using both (34) and (61) as reaction catalyst to give $Me_3SiO\left[(SiMe_2O)_{12}(\overline{SiMe(CH_2)_5CH_3O})\right]_nSiMe_3$ (68).

The compound $\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]_3RhCl$ (35) which is a polymeric analogue of Wilkinson's complex, gave an interesting result when used as a catalyst for the reaction of (22) with 1-hexene. Following gentle refluxing for 1 hour, distillation of the reaction mixture gave the expected hydrosilylation product (65) in 71% yield, and a small quantity of n-hexane. This was formed as a result of (22) serving as a source of hydrogen, and in the presence of a hydrogenation catalyst reduction of 1-hexene to n-hexane occurred. The hydro trisiloxane (22) has been used by Matlin and Gandham[177] for the reduction of aldehydes and ketones in the presence of an organotin catalyst supported on silica. The model rhodium catalyst (35) was also used to good effect in hydrosilylating 1-hexene with triethoxysilane $(EtO)_3SiH$ to give $(EtO)_3Si(CH_2)_5CH_3$ (69) in 73% yield. This hydrosilylation was directly comparable to that achieved by Marciniec et al using $RhCl(PPh_3)_3$ as reaction catalyst where a 74% yield of (69) was achieved.

The pyridine functionalised trisiloxane (25), which was previously prepared from bromide ion substitution in (24) by $LiCH_2C_5H_4N$, was synthesised in high yield from a two hour reaction between (22) and 4-vinylpyridine using (34) as catalyst. The identity of the product was confirmed by comparing its infrared and $^1H/^{13}C$ n.m.r. spectra with those previously described in Chapter 2.

In view of the high catalytic activity of (34) in hydrosilylation reactions, two further reactions employing this catalyst were tried between (22) and allyl functionalised compounds, namely allylisothiocyanate and allylamine, in an attempt to extend our range of model functionalised trisiloxanes. However, even after vigorous refluxing over 24 hours no addition products were formed in either case.

5.4 CATALYTIC PROCEDURES

5.4.1 HYDROGENATION REACTIONS

To a 5 mm n.m.r. tube was added cyclohexene (0.024 g, 0.29 mmol), d_6-benzene (0.3 ml) and $\left[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)\right]_3RhCl$ (35) (0.0065 g, 0.0046 mmol Rh). The tube was cooled to 0°C and the mixture saturated with anhydrous hydrogen gas. The tube was tightly stoppered and then placed in a constant temperature water bath (35°C). At periodic intervals the tube was removed from the water bath, cooled to ambient temperature and the contents analysed by ^1H n.m.r. spectroscopy.

This procedure was similarly employed for the experiments listed in Table 5.1 using (31) (0.005 g, 0.005 mmol Pd), (59) (0.006 g, 0.003 mmol Pd), (62) (0.006 g, 0.002 mmol Rh), and 0.03 ml of ethanol when used as a co-solvent.

A degassed mixture of benzene (1.75 ml), ethanol (0.25 ml) and cyclohexene (0.20 g) were introduced to a 10 ml round bottomed flask which had previously been purged with N_2. To the flask was added (62) (0.012 g, 0.0043 mmol Rh) and the mixture degassed with hydrogen at 0°C for 0.25h before sealing with a septum cap. A hydrogen balloon was connected to the flask via a syringe needle. The flask was immersed in a thermostated water bath, and at periodic time intervals samples were withdrawn and analysed by gas chromatographic analysis.

This procedure was repeated for individual experiments using cyclohexene and benzene/ethanol mixtures as above with (59) (0.012 g, *ca* 0.0065 mmol Pd) as catalyst.

The experiments using allyl alcohol (0.20 g), were in benzene (2 ml) using both (62) (0.009 g, *ca* 0.0032 mmol Rh) and (59) (0.011g, *ca* 0.006 mmol Pd) as catalysts at 60°C.

5.4.2 HYDROSILYLATION REACTIONS

$(Me_3SiO)_2SiMe(CH_2)_5CH_3$ (65)

A mixture of $(Me_3SiO)_2SiMe(H)$ (22) (3.0 g, 13.5 mmol), 1-hexene (2.0 g, 23.8 mmol) and either (34) (0.01 g, 0.01 mmol Rh) or (61) (0.01 g, 0.0046 mmol Rh) as catalyst were heated under N_2 for 1h such that the solution gently refluxed. After cooling, excess olefin was evaporated by pumping in vacuo. The residue was distilled under reduced pressure to yield the product as a colourless oil.

This procedure was similarly employed for the preparations of compounds (66), (67) and (69) using similar reagent quantities, for which analytical data is listed in Table 5.4. For the preparation of (68), the rhodium catalyst (35) (0.0014 g, 1×10^{-5} mol Rh) was used.

Table 5.4 Analytical data[a] for selected hydrosilylation reaction products

Compound		Yield %	B.p.[b] (°C)	Analysis (%) C	H
(65)	$(Me_3SiO)_2SiMe(CH_2)_5CH_3$	68	78(2.5)	50.66(50.98)	10.90(11.11)
(66)	$(Me_3SiO)_2SiMe(CH_2)_7CH_3$	74	98(1.3)	54.24(53.89)	11.60(11.37)
(67)	$(Me_3SiO)_2SiMe(CH_2)_9CH_3$	88	120(1.3)	56.59(56.35)	11.58(11.60)
(69)	$(EtO)_3Si(CH_2)_5CH_3$	73	58(1.0)	57.80(58.06)	11.52(11.29)

[a] Calculated data in parentheses. [b] P/mmHg in parentheses.

$Me_3SiO\left[(SiMe_2O)_{12}(SiMe(CH_2)_5CH_3O)\right]_nSiMe_3$ (68)

To a stirred solution of 1-hexene (1.00 g, 11.9 mmol) and (55) (0.40 g, 0.42 mmol H) was added (34) (0.001 g, 0.001 mmol Rh) at ambient temperature. The mixture was heated and refluxed for 1h before cooling. The viscous solution was pumped in vacuo to eliminate volatiles to leave a colourless oil which appeared analytically pure from spectroscopic evidence.

This compound was prepared by a similar procedure using 1-hexene (1.00 g, 11.9 mmol), (55) (0.25 g, 0.26 mmol H) and (61) (0.0058 g, 0.001 mmol Rh) as reaction catalyst. After a 1h reaction, the mixture was slurried in n-hexane (20 ml) and the catalyst filtered off. The solvent and volatiles were evaporated by pumping in vacuo to yield the product as a viscous colourless oil as above.

$(Me_3SiO)_2SiMe(CH_2CH_2CH_2C_5H_4N)$ (25)

A mixture of (22) (2.00 g, 9.0 mmol), 4-vinylpyridine (2.00 g, 19.4 mmol) and (34) (0.003 g, 0.0029 mmol Rh) were heated under a N_2 atmosphere to 120°C for 2h. After cooling the contents were transferred to a N_2 filled distillation apparatus and distilled in the complete absence of air. The title compound was isolated as a yellow oil (2.9 g, 72%) boiling at 158°C (1.0 mm Hg). The infrared and $^1H/^{13}C$ nuclear magnetic resonance spectra of this compound were found to be identical to those recorded for a sample prepared in 2.5.2.

Hydrosilylation reactions with gas chromatographic analysis:

To (22) (1.0 g, 4.50 mmol) in a one-necked 10 ml round bottomed flask was added 1-hexene (0.75 g, 8.93 mmol). The flask was sealed with a septum cap and then immersed in a thermostated water bath seated over

a magnetic stirrer. After 0.25h, a solution of the catalyst (34) (0.003 g, 0.0029 mmol Rh) in 1-hexene (0.30 g) was added using a syringe and the reaction was timed from this addition. Samples of the reaction mixture were periodically withdrawn and analysed by gas chromatography.

This procedure was similarly used for experiments catalysed by the polymer supported reagent (61) (0.0056 g, 0.0029 mmol Rh), except that the catalyst was placed in the flask above the liquid level before sealing with a septum. When the flask contents had reached the temperature of the water bath, the catalyst was washed into the solution by shaking, and the reactions were timed from this point. Hydrosilylations using both catalysts were carried out at the following temperatures: ambient, 40, 50, 55, 60 and 80^{o}C.

CONCLUSIONS

The use of transition-metal complexes anchored on polymer/solid supports has attracted widespread interest in recent years. Functionalised inorganic solids such as silica, and organic polymers, typically cross-linked polystyrene, have been used to good effect as support matrices. Soluble and liquid supports have received little attention.

In these studies, a series of soluble polyorganosiloxane supports which contain potential metal-ligating entities have been prepared and characterised. The polymers were synthesised from either functionalised dichlorosilanes, or from cyclosiloxanes which were polymerised into linear polysiloxanes and subsequently chemically modified to bear pendant ligand groupings. The metallation reactions were primarily focused on anchoring platinum group residues onto a diphenylphosphine functionalised polymer, which yielded stable supported catalysts having limited solubility in polar organic solvents.

Our initial studies were focused on the preparation of a series of tri-, tetra- and penta-siloxanes which proved invaluable as model compounds for the later syntheses of polysiloxane analogues, both metallated and non-metallated. The non-metallated model siloxanes were all air-stable oils with the exception of the bromine, pyridine and phosphine functionalised compounds which reacted vigorously with oxygen. The metallated containing nickel, palladium and rhodium species bonded to the diphenylphosphine functionalised tri-siloxane were air-stable, whereas other metal-ligand combinations proved unstable at ambient temperatures even under inert atmospheres.

Hydrogenation studies on 1-olefins using $PdCl_2L_2$, $RhClL_3$ where L =

$(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)$, $\{Me_3SiO[(SiMe_2O)_8SiMe(CH_2CH_2PPh_2)O]_nSiMe_3\}_2$ $PdCl_2$ and $\{Me_3SiO[(SiMe_2O)_8SiMe(CH_2CH_2PPh_2)O]_nSiMe_3\}_3RhCl$ as catalysts gave very low conversions to alkane products. Traces of ethanol promoted the reactions, but also caused leaching of the catalyst and hence a loss in catalytic activity.

Hydrosilylation studies on 1-olefins using the hydrido-siloxane $(Me_3SiO)_2SiMe(H)$ were effected in high yield under mild conditions with very low concentrations of two rhodium carbonyl chloride containing catalysts, namely, $[(Me_3SiO)_2SiMe(CH_2CH_2PPh_2)]_2Rh(CO)Cl$ and $\{Me_3SiO[(SiMe_2O)_8SiMe(CH_2CH_2PPh_2)O]_nSiMe_3\}_2Rh(CO)Cl$ (n = ca 25). The terminal hydrosilylation addition product was isolated in each case, and identified by spectroscopic analysis.

The use of polysiloxanes as a support matrix for heterogenising homogeneous catalysts is still in its infancy, and we await with interest the further developments of these compounds in catalytic systems.

APPENDIX I

SAFETY

The toxicological properties of silanes and siloxanes have not been fully investigated, and necessary precautions were taken when using these materials. The reagents involved in this work are commonly used materials, and the precautions taken when handling them were in accordance with their known hazards.

REAGENTS

All chemicals employed were standard laboratory reagents (BDH or AnalaR grade) which were used without further purification unless otherwise stated. All laboratory solvents with the exception of benzene were dried over BDH 4A molecular sieves for at least 24 hours, and deoxygenated with oxygen-free dry nitrogen gas prior to purification and use. Acetone was distilled from anhydrous calcium sulphate, while benzene was dried over sodium wire. Diethyl ether and tetrahydrofuran were freed from peroxides by passing through an alumina column. Diethylether and dichloromethane were distilled from calcium chloride, and thf from calcium hydride.

The silanes $SiMe_3Cl$, $SiMeCl_2H$, $SiMeCl_2(CH{=}CH_2)$ and $SiMeCl_2(CH_2CH{=}CH_2)$ were commercial samples from Aldrich Chemical Company, and were used directly without further purification.

$LiPPh_2$,[178] LiC_5H_5[87], $LiCH_2C_5H_4N$[179] and NaC_5H_5[180] were prepared by literature methods.

APPENDIX II

INSTRUMENTATION

INFRARED SPECTRA

4000 - 200 cm^{-1}

Infrared spectra in this region were recorded on either a Perkin-Elmer 5776 or 5996 spectrophotometer. Samples were prepared as neat oils or nujol mulls using NaCl discs, or as solutions in cyclohexane in a Beckmann RIIC FS 125 0.1 mm NaCl cell. For the far infrared region, (600 - 200 cm^{-1}), neat oils or nujol mulls were held between CsI discs.

NUCLEAR MAGNETIC RESONANCE (n.m.r.)

^{1}H (proton)

Proton n.m.r. were recorded on a Hitachi Perkin-Elmer R-24B (60 MHz) or a JEOL PS 100 spectrometer. The samples were prepared using deuterated chloroform or benzene as solvents unless otherwise stated, with tetramethylsilane (TMS) or dichloromethane as internal standards.

^{13}C (carbon)

^{13}C n.m.r. were recorded on a JEOL FX 90Q FT n.m.r. spectrometer. The samples were prepared using deuterated chloroform or benzene as solvents unless otherwise stated, with tetramethylsilane or deuterochloroform as internal standards.

^{29}Si (silicon)

^{29}Si n.m.r. were recorded using a Bruker WH 400 spectrometer care of the Department of Chemistry and Molecular Sciences, University of Warwick. The samples were prepared using deuterochloroform.

MASS SPECTRA

Mass spectra were recorded on a VG 70 70E instrument equipped with a DS 2025 data system using direct insertion probes and ionising energies of 12 and 70 eV. C.I. spectra were also obtained for compounds which did not show molecular ions under these conditions.

ANALYSES

Carbon, hydrogen, bromine, chlorine, nitrogen, phosphorus and rhodium analyses were determined by microanalytical techniques care of Butterworth Laboratories, Teddington, Middlesex, and Analytical Services, School of Chemistry, University of Bath.

GEL PERMEATION CHROMATOGRAPHY (G.P.C.)

G.P.C. studies were carried out on a Knauer HPLC pump 64 and a Knauer differential refractometer. Analytical studies were on 30 cm PL-Gel 5 m mix and 10 m mix columns, with preparative runs on a 60 cm PL-Gel 10 m mix column. AnalaR toluene was the solvent used in all G.P.C. work. The flow rate for analytical studies was 1 ml min^{-1} with injection volumes of 10 μl for sample concentrations of 5% w/w. For preparative work, the flow rate was 9.9 ml min^{-1} with injection volumes of 2000 μl. The sample concentration was dependent on sample solubility.

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Syntheses of Organofunctional Siloxanes containing Metal-ligating Side-chains†

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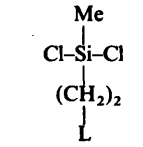
A range of tri-, tetra-, and penta-siloxanes of general formula $Me_3SiO[SiMe(R)O]_nSiMe_3$ (R = vinyl, n = 1—3; R = an alkyl chain terminated by the potential metal-ligating entities $CH{=}CH_2$, Ph, CN, cyclohexenyl, pyridine, and PPh_2, n = 1 or 2) have been synthesised from commercially available dichlorosilanes by one of three procedures. The products are air-stable oils with the exception of the pyridine- and phosphine-functionalised compounds which react vigorously with oxygen, and the spectroscopic properties of corresponding organofunctional siloxanes are very similar showing little dependence on n.

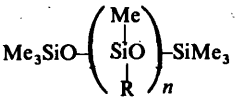
The concept of attaching transition-metal species to solid supports to produce catalysts which combine the versatility, selectivity, and reproducibility of homogeneous catalysts with the separation advantages of heterogeneous systems has attracted widespread interest.[1–3] Many solid polymeric organic materials, modified to bear pendant metal-binding entities, have been used to anchor catalytically active metal species,[1–5] but all such systems exhibit limited thermo-oxidative stability, and most suffer from lack of chemical reproducibility. Of the solid, inorganic supports available, silica and its minerals have received most attention. Metal species are usually attached *via* ligating groups which are chemically bonded to the solid *via* surface silanol reactions, but again reproducibility and precise determination of the degree of surface modification and metallation are difficult to establish.[6–8]

The ideal supported catalyst should combine the thermal stability of inorganic supported systems with the beneficial attributes of homogeneous catalysts. We believe that thermally stable, macromolecular liquid supports offer many advantages over conventional solid support systems, and therefore warrant further attention. For example, reactions on substrates miscible with such a polymer could be carried out in a liquid phase devoid of conventional solvents, and thus suitable for use over a wide range of temperature and pressure. In addition many of the separation problems encountered in homogeneous catalysis could also be circumvented by bonding the catalytically active metal centres to such a support. Of the various liquid polymers available, those based on linear or cyclic polysiloxanes are prime candidates for such an examination. These materials are chemically robust, thermally stable, readily available, and capable of systematic structural modification.[9] In order to bind metal entities to the polymer in a regular and well defined way, it is necessary to have available a range of synthetic procedures for introducing various functional groups into the polymer. In this paper we describe the synthesis of a range of functionalised tri-, tetra-, and penta-siloxanes, containing respectively one, two, or three identical substituents capable of binding metal entities, which will serve as models for future syntheses and investigations of long-chain organofunctional polysiloxanes.

Results and Discussion

The compounds $SiMeCl_2H$ and $SiMeCl_2(CH{=}CH_2)$ have been used to prepare the dichlorosilanes (1)—(4) for conversion





	L		n	R		n	R
(1)	Ph	(5)	1	$(CH_2)_2Ph$	(16)	1	$CH_2CH{=}CH_2$
(2)	CH_2Ph	(6)	2	$(CH_2)_2Ph$	(17)	2	$CH_2CH{=}CH_2$
(3)	CH_2CN	(7)	1	$(CH_2)_3Ph$	(18)	1	$(CH_2)_2Br$
(4)	C_6H_9 (cyclohexenyl)	(8)	2	$(CH_2)_3Ph$	(19)	1	$(CH_2)_3C_5H_4N$
		(9)	1	$(CH_2)_3CN$	(20)	1	$(CH_2)_2PPh_2$
		(10)	2	$(CH_2)_3CN$	(21)	2	$(CH_2)_2PPh_2$
		(11)	1	$(CH_2)_2C_6H_9$	(22)	1	$(CH_2)_3PPh_2$
		(12)	2	$(CH_2)_2C_6H_9$			
		(13)	1	$CH{=}CH_2$			
		(14)	2	$CH{=}CH_2$			
		(15)	3	$CH{=}CH_2$			

into the majority of the organofunctional siloxanes $Me_3SiO[SiMe(R)O]_nSiMe_3$ listed above [compounds (5)—(22)]. The syntheses have followed one of three routes. In the first of these, chemical modification of dichloromethylvinylsilane is followed by hydrolysis in the presence of chlorotrimethylsilane [equation (1)]. Under Friedel Crafts conditions, anti-Markownikoff

$$MeSiCl_2(CH{=}CH_2) \xrightarrow{HL} MeSiCl_2(CH_2CH_2L) \xrightarrow[H_2O]{Me_3SiCl} Me_3SiO[SiMe(CH_2CH_2L)O]_nSiMe_3 \quad (1)$$
$$(L = Ph, n = 1 \text{ or } 2)$$

addition of benzene across the vinyl group of $SiMeCl_2(CH{=}CH_2)$ readily occurs to yield $SiMeCl_2(CH_2CH_2Ph)$ as a moisture-sensitive colourless oil. Only the terminal adduct is formed in this reaction, but under similar conditions alkyl-substituted arenes such as toluene or mesitylene react to form a mixture of several chlorosilanes from which the required terminal product could not be isolated in a pure state.

An alternative procedure involving the platinum-catalysed hydrosilylation of 1-alkenes proved more versatile for the synthesis of a larger range of pure analogues [equation (2)].

$$MeSiCl_2H + CH_2{=}CHL \xrightarrow{\text{catalyst}} MeSiCl_2(CH_2CH_2L) \downarrow Me_3SiCl, H_2O$$
$$Me_3SiO[SiMe(CH_2CH_2L)O]_nSiMe_3 \quad (2)$$
$$(L = CH_2CN, CH_2Ph, \text{or } C_6H_9; n = 1 \text{ or } 2)$$

† *Non-S.I. units employed:* eV ≈ 1.60 × 10^{-19} J, mmHg ≈ 133 Pa.

Table 1. Analytical data[a] for siloxane derivatives

Compound	Yield		B.p.[b] (°C)	Analysis (%)	
	n	%		C	H
(5) $Me_3SiO[SiMe(CH_2CH_2Ph)O]_nSiMe_3$	1	33	116 (0.1)	54.9 (55.1)	9.15 (9.20)
(6)	2	24	198 (0.8)	57.8 (58.8)	8.65 (8.55)
(7) $Me_3SiO[SiMe(CH_2CH_2CH_2Ph)O]_nSiMe_3$	1	57	106 (0.1)	56.7 (56.5)	8.90 (9.40)
(8)	2	19	192 (0.2)	59.6 (60.2)	8.80 (8.90)
(9) $Me_3SiO[SiMe(CH_2CH_2CH_2CN)O]_nSiMe_3$	1	22	106 (1.2)	44.5 (45.5)	9.05 (9.35)
(10)	2	11	194 (3.1)	45.4 (46.2)	8.90 (8.65)
(11) $Me_3SiO[SiMe(CH_2CH_2C_6H_9)O]_nSiMe_3$	1	50	92 (0.2)	53.0 (54.5)	10.5 (10.3)
(12)	2	23	172 (0.2)	56.8 (57.8)	10.4 (10.0)
(13) $Me_3SiO[SiMe(CH{=}CH_2)O]_nSiMe_3$	1	12	46 (1.2)	43.4 (43.5)	9.30 (9.65)
(14)	2	40	82 (1.3)	43.1 (43.1)	8.85 (9.00)
(15)	3	32	97 (1.3)	43.2 (42.9)	8.75 (8.55)
(16) $Me_3SiO[SiMe(CH_2CH{=}CH_2)O]_nSiMe_3$	1	36	29 (0.1)	44.1 (45.8)	9.95 (9.90)
(17)	2	8	54 (0.01)	43.6 (46.4)	9.70 (9.40)

[a] Calculated data in parentheses. [b] *P*/mmHg in parentheses.

Table 2. Proton and ^{13}C n.m.r. data for selected siloxanes*

	Me_3SiO	SiMe	C^1/H^1	C^2/H^2	C^3/H^3	Others	Aromatics
(5)	0.10 (18 H, s)	0.10 (3 H, s)	0.80 (2 H, m)	2.64 (2 H, m)			7.18 (5 H, m)
	1.90	−0.27	19.8	29.4			145.1, 128.3, 127.9, 125.5
(7)	0.07 (18 H, s)	0.07 (3 H, s)	0.45 (2 H, m)	1.60 (2 H, m)	2.58 (2 H, m)		7.12 (5 H, m)
	−0.19	−0.10	17.5	25.2	39.5		142.7, 128.5, 128.3, 125.7
(9)	0.54 (18 H, s)	0.48 (3 H, s)	1.04 (2 H, m)	2.13 (2 H, m)	2.80 (2 H, m)		
	1.54	−0.57	16.8	19.8	20.2	119.3 (CN)	
(11)	0.08 (18 H, s)	0.08 (3 H, s)	0.48 (2 H, m)	1.30 (2 H, m)		1.80 (7 H, m),	
	1.57	−0.32	14.7	30.3		5.64 (2 H, m)	127.0, 126.7, 36.4, 31.8, 28.7, 25.5
(13)	0.46 (18 H, s)	0.46 (3 H, s)	6.25 (3 H, m)	132.0			
	2.31	0.00	137.5				
(16)	0.12 (18 H, s)	0.12 (3 H, s)	1.51 (2 H, d)	5.80 (1 H, m)	4.88 (2 H, m)		
	2.71	0.01	26.7	135.0	114.5		
(18)	0.54 (18 H, s)	0.54 (3 H, s)	1.74 (2 H, m)	3.94 (2 H, m)			
	1.84	0.49	25.1	30.1			
(19)	0.50 (18 H, s)	0.05 (3 H, s)	0.46 (2 H, m)	1.65 (2 H, m)	2.58 (2 H, t)		7.02 (2 H, d), 8.41 (2 H, d)
	0.16	0.00	17.4	24.3	38.7		151.4, 149.9, 124.1
(20)	0.80 (18 H, s)	0.80 (3 H, s)	0.56 (2 H, m)	2.02 (2 H, m)			7.28 (5 H, m)
	1.90	−0.49	13.2 (d, 9.8)	21.0 (d, 14.7)			139.2 (d, 13.7), 134.0 (d, 17.1), 132.8 (d, 18.3), 128.3 (d, 3.7)
(22)	0.06 (18 H, s)	0.06 (3 H, s)	0.67 (2 H, m)	1.54 (2 H, m)	2.12 (2 H, m)		7.38 (5 H, m)
	2.06	0.22	19.7 (d, 10.3)	19.9 (d, 12.7)	32.7 (d, 13.1)		139.4 (d, 13.1), 134.1 (d, 17.1), 132.9 (d, 17.1), 128.5 (d, 3.7)

* Carbon chain numbered from the Si atom.

Only the required terminal dichlorosilanes were formed in this reaction, with no n.m.r. evidence of CH or CH_3 moieties produced by internal addition. Siloxanes were prepared by co-hydrolysis of the appropriate organofunctional dichlorosilane and chlorotrimethylsilane in diethyl ether–water mixtures, and provided this reaction was carried out at low temperature, the HCl liberated on hydrolysis did not cause significant cleavage of Si–O bonds. Hexamethyldisiloxane was formed as a by-product in each reaction, but the separation of the two series of siloxanes ($n = 1$ and $n = 2$) from the reaction mixture was readily achieved by fractional distillation under reduced pressure (Table 1). A third member of the series ($n = 3$) was isolated in a pure state only for the vinyl-functionalised siloxanes. A similar hydrolytic procedure has been used previously by Brzezinska and Cullen[10] in the preparation of $Me_3SiO[SiMe(CH{=}CH_2)O]_nSiMe_3$ ($n = 1$ or 3) from $SiMeCl_2(CH{=}CH_2)$, but they were unable to isolate the analogue with $n = 2$, which was the major product under our reaction conditions.

The remaining siloxanes were prepared from other organofunctional siloxanes either by substitution of the halogen in compound (**18**) or by addition across the carbon–carbon double bond in (**13**), (**14**), or (**16**) as shown in equations (3)—(5). Although the pyridine derivative (**19**) was readily

$$Me_3SiOSiMe(CH_2CH_2Br)OSiMe_3 \xrightarrow{LiCH_2C_5H_4N} Me_3SiOSiMe(CH_2CH_2CH_2C_5H_4N)OSiMe_3 \quad (3)$$

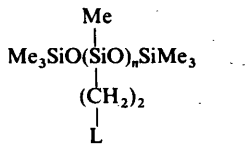
$$Me_3SiO[SiMe(CH{=}CH_2)_n]_nSiMe_3 \xrightarrow[h\nu]{PHPh_2} Me_3SiO[SiMe(CH_2CH_2PPh_2)O]_nSiMe_3 \quad (4)$$
$$(n = 1 \text{ or } 2)$$

$$Me_3SiOSiMe(CH_2CH{=}CH_2)OSiMe_3 \xrightarrow[h\nu]{PHPh_2} Me_3SiOSiMe(CH_2CH_2CH_2PPh_2)OSiMe_3 \quad (5)$$

formed by treating $Me_3SiOSiMe(CH_2CH_2Br)OSiMe_3$ with $LiCH_2C_5H_4N$ in tetrahydrofuran (thf), attempts to prepare phosphinated siloxanes by reaction of compound (**18**) with

$Li[PPh_2]$ or $Na[PPh_2]$ were unsuccessful under any of the reaction conditions tried, and resulted instead in cleavage of Si–O bonds and degradation of the trisiloxane backbone. Interestingly, this reaction has been carried out successfully on both chloromethylated polyphenylsiloxanes[11] and halogen-containing polymethylsiloxanes,[12] without, apparently, any such degradation problems. Since the photochemical addition of Ph_2PH to vinyl-functionalised tri- or tetra-siloxanes or to the allyl-functionalised trisiloxane (**16**) gave the required phosphinated derivatives (**20**)—(**22**) in high yields, attempts to prepare these compounds by halogen substitution were abandoned.

All the siloxane derivatives are air-stable oils with the exception of the pyridine- and phosphine-functionalised compounds (**19**) and (**20**)—(**22**) which are readily oxidised, the latter three being pyrophoric. Spectroscopic data on the three series of complexes (**A**)—(**C**) are very similar, and we were able to detect



[n = 1 (**A**); n = 2 (**B**); n = 3 (**C**)]

signs of separate n.m.r. signals for the two or four diastereoisomers expected for compounds of types (**B**) or (**C**), repectively only for compounds (**6**) and (**10**), and then only in the MeSi region of their ^{13}C n.m.r. spectra additional shoulders were observed compared with the spectra of compounds of type (**A**), data for which are given in Table 2. Compounds (**5**)—(**22**) all show strong i.r. absorptions characteristic[13,14] of methylsiloxanes at *ca.* 2 940 (C–H str.) 1 430 (C–H bend), 1 410 and 1 270 (CH_3 asym. and sym. deformations), and 1 100—1 000 cm^{-1} (Si–O–Si asym. str.) in addition to bands typical of the functional group (R) in each individual compound.

Mass Spectral Data.—With a few exceptions the literature on the mass spectra of siloxanes is limited to studies on small cyclic and long-chain linear siloxanes,[15–17] consequently the mass spectra of the more volatile siloxanes prepared in this study [type (**A**), compounds (**5**), (**7**), (**9**), (**11**), (**13**), (**16**), (**18**), and (**20**)] have been obtained. In each spectrum the molecular ion $M^{\cdot+}$ is very weak or entirely absent [although $(M + H)^+$ is clearly seen in chemical ionisation (c.i.) spectra], and facile loss of Me$^{\cdot}$ or R$^{\cdot}$ is reflected in the high intensities of the $(M - Me)^{\cdot+}$ and $(M - R)^{\cdot+}$ peaks. Other common fragments observed include those due to $(M - R - CH_2)^+$, $(Me_3SiOSiMe_2)^+$, Me_2SiR^+, and Me_3Si^+, and indicate a similar fragmentation mechanism for all compounds irrespective of the nature of R, with the single exception of compound (**18**) where simple Me$^{\cdot}$ loss from the parent molecular ion is not observed. Doubly charged ions have been observed previously in other studies on methylsiloxanes,[16] and weak $(M - 2Me)^{2+}$ ions occur in the spectra of compounds (**9**), (**13**), (**16**), and (**20**). The remaining intense ions in the mass spectra of (**9**), (**13**), and (**18**) with m/z = 246, 205, and 287, respectively, result from the loss of ethene and Me$^{\cdot}$ (43 mass units) from their molecular ions, and for (**16**) the ion with m/z = 205 corresponds to loss of propene and Me$^{\cdot}$ (57 mass units) from the molecular ion.

Experimental

All work with air-sensitive materials was carried out in a dry, oxygen-free atmosphere using freshly distilled, deoxygenated solvents. I.r. spectra were measured on a Perkin-Elmer 599b spectrometer. Proton and $^{13}C-\{^1H\}$ n.m.r. spectra were recorded with JEOL PS 100 and FX 90Q spectrometers respectively, using $CDCl_3$ as solvent unless otherwise stated. Data given are for room-temperature measurements, and chemical shifts are given in p.p.m. downfield from internal $SiMe_4$. Mass spectra were recorded on a VG 70 70E instrument using direct-insertion probes and ionising energies of 12 and 70 eV, and for compounds which did not show molecular ions under these conditions c.i. spectra were also obtained. Analyses were by Butterworth Laboratories Ltd.

The silanes $SiMe_3Cl$, $SiMeCl_2H$, $SiMeCl_2(CH{=}CH_2)$, and $SiMeCl_2(CH_2CH{=}CH_2)$ were commercial samples used as received; $LiCH_2C_5H_4N$ was prepared from 4-methylpyridine by literature methods.[18]

Syntheses.—$SiMeCl_2(CH_2CH_2Ph)$ (**1**). Anhydrous $AlCl_3$ (0.36 g, 2.7 mmol) was added to a solution of dichloromethylvinylsilane (10.0 g, 70.9 mmol) in benzene (11.0 g, 0.14 mmol) and the mixture heated under reflux for 1 h. After cooling to 0 °C, the mixture was filtered and the filtrate treated with NEt_3 (0.3 cm^3) in order to complex undissolved $AlCl_3$. A further small quantity of solid was removed by filtration and the filtrate distilled under reduced pressure, yielding compound (**1**) as a colourless oil (9.8 g, 63%), b.p. 89 °C (0.5 mmHg) (Found: C, 48.2; H, 5.60; Cl, 30.6. $C_9H_{12}Cl_2Si$ requires C, 49.3; H, 5.50; Cl, 32.4%). N.m.r. ($CDCl_3$): ^1H, 7.2 (m, 5 H, aromatic H), 2.81 (m, 2 H, CH_2Ph), 1.42 (m, 2 H, $SiCH_2$), and 0.64 (s, 3 H, Me); ^{13}C, 142.3, 128.5, 127.8, 126.1 (aromatics), 28.5 (CH_2Ph), 23.4 ($SiCH_2$), and 5.2 (Me).

The compound $SiMeCl_2(CH_2CH_2CH_2Ph)$ (**2**) was prepared in 70% yield by the procedure described by Musolf and Speier,[19] while $SiMeCl_2(CH_2CH_2CH_2CN)$ (**3**) and $SiMeCl_2(CH_2CH_2C_6H_9)$ (**4**) were synthesised from $SiMeCl_2H$ in yields of over 80% by literature methods.[20]

$Me_3SiO[SiMe(CH_2CH_2Ph)O]_nSiMe_3$ (n = 1 *or* 2). A solution of $SiMeCl_2(CH_2CH_2Ph)$ (10.2 g, 46.6 mmol) and $SiMe_3Cl$ (10.1 g, 93.2 mmol) in Et_2O (25 cm^3) was added dropwise with stirring to water (20 cm^3) cooled in ice. The stirred mixture was allowed to warm to ambient temperature over 1 h. The ether layer was separated, dried, and the solvent removed *in vacuo*. Distillation of the residual oil under reduced pressure yielded compounds (**5**) and (**6**) as colourless oils (Table 1). Higher siloxanes remained undistilled.

By an analogous procedure using a 2:1 mole ratio of $SiMe_3Cl$ to dichlorosilane derivative, a range of siloxanes was produced [(**7**)—(**17**), Table 1].

$Me_3SiOSiMe(CH_2CH_2Br)OSiMe_3$ (**18**). A slow stream of anhydrous HBr was passed through compound (**16**) (14.8 g, 59.6 mmol) containing a catalytic quantity of benzoyl peroxide (0.1 g). An exothermic reaction occurred and the temperature of the solution increased to 35—40 °C. Reaction was assumed to be complete when the solution temperature returned to ambient. Fractionation under reduced pressure yielded compound (**18**) as a colourless oil (17.2 g, 88%), b.p. 74 °C (1.3 mmHg) (Found: C, 33.1; H, 7.35; Br, 27.5. $C_9H_{25}BrO_2Si_3$ requires C, 32.8; H, 7.60; Br, 24.3%).

$Me_3SiOSiMe(CH_2CH_2CH_2C_5H_4N)OSiMe_3$ (**19**). A solution of $LiCH_2C_5H_4N$ (7.78 g, 1.81 mmol) in thf (15 cm^3) was added dropwise with rapid stirring to a solution of compound (**18**) in thf (15 cm^3). The mixture was stirred for 3 d prior to distillation in the complete absence of oxygen. The product was isolated as a yellow, air-sensitive oil (4.7 g, 76%), b.p. 122 °C (0.25 mmHg) (Found: C, 51.9; H, 9.2; N, 3.60. $C_{15}H_{31}NO_2Si_3$ requires C, 52.8; H, 9.1; N, 4.00%).

$Me_3SiOSiMe(CH_2CH_2PPh_2)OSiMe_3$ (**20**). A mixture of compound (**13**) (4.00 g, 1.61 mmol) and $PHPh_2$ (2.50 g, 1.34 mmol) was sealed under a N_2 atmosphere in a thick-walled Pyrex tube (50 cm^3). The tube was irradiated with light from a

400-W mercury lamp for 48 h while the contents were continuously stirred. On completion of the reaction the product was isolated as a colourless, air-sensitive oil (5.5 g, 79%) by distillation under reduced pressure (b.p. 178 °C at 0.9 mmHg) (Found: C, 58.7; H, 8.00; P, 6.95. $C_{21}H_{35}O_2PSi_3$ requires C, 58.1; H, 8.05; P, 7.15%).

$Me_3SiO[SiMe(CH_2CH_2PPh_2)O]_2SiMe_3$ (**21**). This compound was isolated as an air-sensitive oil in almost quantitative yield on irradiation of (**14**) (1.72 g, 5.14 mmol) and $PHPh_2$ (1.91 g, 10.3 mmol) as above. Distillation without decomposition did not prove possible, but the oil appeared analytically pure after pumping *in vacuo* (0.01 mmHg) and there was no spectroscopic evidence for unreacted starting materials (Found: C, 60.4; H, 7.40; P, 8.60. $C_{36}H_{52}O_3P_2Si_4$ requires C, 61.2; H, 7.35; P, 8.80%).

$Me_3SiOSiMe(CH_2CH_2CH_2PPh_2)OSiMe_3$ (**22**). This compound was prepared by a similar procedure to that used for (**20**), from (**16**) (2.00 g, 7.63 mmol) and $PHPh_2$ (1.18 g, 6.34 mmol), and was isolated as an air-sensitive, colourless oil (2.1 g, 58%), b.p. 190 °C (0.1 mmHg) (Found: C, 59.6; H, 7.90; P, 7.60. $C_{22}H_{37}O_2PSi_3$ requires C, 58.9; H, 8.25; P, 6.90%).

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